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THE HWIR SURFACE WATER MODULE

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1.0 INTRODUCTION

The HWIR Surface Water Module is one component of a software system that is designed to evaluate the nationwide probability of human and ecological risk from chemicals placed in various waste management units (WMUs). This new risk assessment software system, the 3MRA, implements a Monte-Carlo approach in which the source, media, exposure, and risk modules are executed repeatedly for a representative set of sites around the country. Many model parameters describing each site are drawn from regional or national distributions. The goal is to simulate a realistic set of sites, not necessarily to represent the actual sites in every detail. The methodology, then, is site-based rather than site-specific. The models chosen and the assumptions incorporated into the simulations reflect this goal and the constraints inherent in a large Monte-Carlo implementation.

Chemical mass released from a WMU can enter a nearby surface water body network in runoff and erosion directly from the WMU, from atmospheric deposition to the water surface, in runoff and erosion from adjoining watershed subbasins, and by interception of contaminated groundwater. The chemical is then subject to transport and transformation processes occurring within the water body network, resulting in variable chemical concentrations in the water column and in the underlying sediments. These chemical concentrations are the basis for direct exposure to human and ecological receptors and indirect exposure through uptake in the aquatic food web.

The HWIR Surface Water Module takes the loadings calculated by the source, atmospheric, watershed, and groundwater modules, along with data on meteorology, hydrology, environmental conditions, and chemical reactivity, and calculates the chemical concentrations throughout the water body network over time. The HWIR Surface Water Module consists of the core model EXAMS II (Burns, 1997, Burns et al., 1982) and the interface module ExamsIO, which is documented here. EXAMS is a general surface water fate model for organic chemicals. This compartment model has been used routinely by both EPA and industry analysts for the analysis of expected pesticide concentrations in generically-defined environments, such as farm ponds. It has also been used for site-specific analysis of pesticide concentrations in various water bodies around the world. The interface module ExamsIO was developed specifically for this HWIR project. It reads data from other HWIR modules and databases, and builds EXAMS input files describing the water body environment and chemical properties, along with the command file that specifies the chemical loading history and controls the EXAMS simulation. ExamsIO passes control to EXAMS, which conducts the simulation and produces intermediate results files. ExamsIO then processes the intermediate files and passes the output data back to the proper HWIR database.

While the EXAMS component of the HWIR Surface Water Module is a fully functional model independent of this project, it is driven and constrained in various ways by ExamsIO and the HWIR databases. For convenience, the HWIR Surface Water Module will be referred to here as H-Exams. This composite module is documented in Chapter 2. The full capabilities of EXAMS are explained in the referenced manuals, and summarized below.

1.1 Summary of EXAMS

EXAMS II is an interactive modeling system that allows a user to specify and store the properties of chemicals and ecosystems, modify either via simple commands, and conduct rapid evaluations and sensitivity analyses of the probable aquatic fate of synthetic organic chemicals. EXAMS combines chemical loadings, transport, and transformation into a set of differential equations using the law of conservation of mass as an accounting principle. It accounts for all the chemical mass entering and leaving a system as the algebraic sum of external loadings, transport processes that export the compound from the system, and transformation processes within the system that convert the chemical to daughter products. The program produces output tables and simple graphics describing chemical exposure, fate, and persistence.

EXAMS represents each waterbody via a set of segments or distinct zones in the system. The program is based on a series of mass balances for the segments that give rise to a single differential equation for each segment. Working from the individual transport and transformation process equations, EXAMS compiles an overall equation for the net rate of change of chemical concentration in each segment. The resulting system of differential equations describes the mass balance for the entire system, which is then solved by the method of lines. EXAMS includes a descriptor language that simplifies the specification of system geometry and connectedness.

EXAMS includes process models of the physical, chemical, and biological phenomena governing the transport and fate of compounds. Each of the unit process equations used to compute the kinetics of chemicals accounts for the interactions between the chemistry of a compound and the environmental forces that shape its behavior in aquatic systems. This "second-order" or "system-independent" approach lets one study the fundamental chemistry of compounds in the laboratory and then, based on independent studies of the levels of driving forces in aquatic systems, evaluate the probable behavior of the compound in systems that have never been exposed to it. Most of the process equations are based on standard theoretical constructs or accepted empirical relationships. The user can specify reaction pathways for the production of transformation products of concern, whose further fate and transport can then be simultaneously simulated by EXAMS.

EXAMS contains process modules for several chemical reactions. Equilibrium reactions are used for sorption and ionization. Kinetic reactions are used for volatilization, hydrolysis (acid, base, and neutral), biodegradation (water column and sediments), photolysis, oxidation, and reduction. EXAMS uses these modules as determined by the input chemical properties. EXAMS has been designed to accept standard water quality parameters and system characteristics that are commonly measured by limnologists throughout the world, and chemical datasets conventionally measured or required by EPA regulatory procedures.

The contaminant fate algorithms in EXAMS include sorption to suspended solids, biotic solids, and sediment solids, but EXAMS does not simulate a solids balance. Solids concentrations

are specified as input data. The effects of settling and resuspension on chemical fate are accounted for in a bulk sediment-water exchange term.

EXAMS can be run in three modes: steady-state, quasi-dynamic with steady environmental data, and quasi-dynamic with monthly environmental data. H-Exams implements mode 2, in which the model integrates the equations over specified time periods with given environmental and loading conditions. Pulse loadings are allowed by EXAMS in mode 2 simulations, but this capability is not implemented by H-Exams. The EXAMS simulation proceeds in yearly increments using yearly-average loadings and environmental conditions.

While EXAMS can be run interactively or as a batch program, H-Exams is implemented solely as a batch process. H-Exams does not consider transformations due to photolysis or oxidation. Transformation rate constants for hydrolysis, biodegradation, and reduction are calculated by the HWIR chemical processor and passed through the batch chemical database to EXAMS. Internal EXAMS algorithms for calculating rate constants are bypassed.

EXAMS incorporates a few major assumptions. The model was designed to evaluate the consequences of longer-term, primarily time-averaged chemical loadings that ultimately result in trace-level contamination of aquatic systems. EXAMS generates a steady-state, average flow field (long-term or monthly) for the ecosystem. The program cannot then fully evaluate the transient, high concentrations that arise from chemical spills, although spills under average hydrological conditions can be studied. An assumption of trace-level chemical concentrations was used to design the process equations. The chemical is assumed not to radically change the environmental variables that drive its transformations. EXAMS uses linear sorption isotherms, and second-order (rather than Michaelis-Menten-Monod) expressions for biotransformation kinetics, which is known to be valid for low concentrations of pollutants. Sorption is treated as a thermodynamic or constitutive property of each compartment in the system, that is, sorption-desorption kinetics are assumed to be rapid compared to other processes. While this assumption may be violated by extensively-sorbed chemicals, they tend to be captured by benthic sediments, where their release to the water column is controlled by benthic exchange processes.

1.2 Summary of ExamsIO

ExamsIO provides the link between other HWIR modules and databases and the EXAMS model. In an HWIR analysis of a particular chemical, several multimedia simulations are set up and executed. Each of these simulations describes a particular site, and proper site simulation files (SSFs) are generated detailing the chemical properties and the site characteristics. The source and natural media modules are then executed, followed by the exposure and risk modules. Modules produce time series calculations and store results in their global results files (GRFs). ExamsIO reads results generated by the source module, the atmospheric module, the watershed module, and the aquifer module. Batch EXAMS files are created, and EXAMS is executed, generating the

temporary results file hwirexp.xms. ExamsIO reads this file and produces the properly named and formatted surface water GRF, which is used as input by the HWIR exposure modules.

Three batch EXAMS files are generated by ExamsIO – the run file “hwirexp.exe,” the chemical file “hwirexp1.chm,” and the environment file “hwirexp.env.” If two or more chemicals are included in one simulation, then separate files are created for each chemical (hwirexp2.chm, hwirexp3.chm, etc.).

The chemical file specifies the relevant chemical properties, including molecular weight, melting point, Henry’s Law constant, vapor pressure, ionization constants, partition coefficients, solubilities, various rate constants, and reaction yield coefficients when appropriate. The environment file specifies all relevant aspects of the physical environment to be simulated. These properties include compartment geometry, advective flow paths, mixing characteristics, and environmental characteristics that influence chemical reactions, such as pH, DOC, microbial activity, and reductant concentration. The run file controls the EXAMS simulation. It sets simulation control variables at the beginning, then specifies yearly inflows and loadings for each modeled compartment. Yearly changes in various environmental properties are also specified, including TSS and water temperature.

1.3 Assumptions and Limitations

The basic model EXAMS incorporates a set of assumptions, as summarized at the end of section 1.1. In addition, the implementation of H-Exams employs several simplifications in order to meet HWIR project requirements and constraints. The project design calls for repeated long simulations (200 to 10,000 years) executed quickly (seconds to minutes). This requirement limits the temporal resolution at which simulations can be conducted. Another important constraint is limited site-specific data. This constraint limits the accuracy with which a particular site can be described. The major model simplifications made in response to these project constraints include the use of average-yearly hydrological and loading inputs, the use of national distributions to specify some site-specific environmental conditions, and the use of a simple solids balance with no settling and burial. For sites that experience periodic drying, a small positive flow equivalent to 5 mm/year of direct precipitation onto the water body surface is maintained in order to keep the model functioning.

These simplifications lead to a degree of model error in the calculated concentrations. Using annual-average loadings and flows rather than daily loadings and flows will lead to calculated annual-average concentrations that are biased somewhat high, depending on the correlation between flow and loading at a particular site. This bias is somewhat mitigated for reactive and volatile chemicals where the loss rate is proportional to the concentration. The use of national distributions rather than site-specific environmental data could cause calculated concentrations to be low or high at a given location, with no known general bias. The simple solids balance will overestimate suspended solids concentrations slightly in streams and more

significantly in ponds, wetlands, and lakes. Calculated total water column chemical concentrations will be high, while the dissolved chemical fraction will be low. The net result for dissolved water column chemical concentrations, which are used for fish exposure, is not expected to be biased significantly high or low.

The procedure for preventing drying of surface water reaches is more difficult to evaluate. This procedure conducts chemical loads downstream within a remnant aquatic reach rather than within runoff over a dry bed or subsurface flow within the bed. While the mass balance is maintained, the chemical and solids concentrations will tend to be elevated within the remnant reach. These elevated concentrations are probably realistic for years in which evaporation exceeds all hydrologic inflows.

2.0 THEORETICAL FRAMEWORK

H-Exams must automatically construct and execute a simulation for each water body system at a site using the HWIR databases that are generated by each Monte-Carlo iteration in a FRAMES-HWIR implementation. The general steps in a simulation are to construct a proper water body network, conduct a water balance, conduct a solids balance, and calculate chemical transport and fate. These steps are detailed in the following sections.

2.1 Water Body Network

Each Monte-Carlo iteration represents a unique site covering an area 2 kilometers in radius from a waste management unit. One or more contiguous water body networks may be located within this area of concern. For each of the 202 HWIR sites around the continental United States, water body networks were defined using the EPA reach file system supplemented with digital elevation modeling. Each water body network is divided into reaches, which are characterized and stored in the site data base. For each Monte-Carlo iteration, proper site definition data are written to file SL.ssf for use by H-Exams. For each separate water body at a site, additional water body data are written to file SW*.ssf, where * is the water body network number (i.e., 1, 2, 3, ...).

A water body network may be composed of a single reach, such as a seepage lake, or several connected reaches, such as a typical dendritic stream drainage system. Reaches are numbered and characterized as to network type (WBNRchType = headwaters, exiting, or other), water body type (WBNRchBodyType = stream, wetland, pond, lake, or bay), reach order (WBNRchOrder = 1, 2, 3, ...), upstream reach numbers (WBNRchRchIndex), and adjacent watershed subbasin numbers (WBNRchWSSubIndex).

For each water body network, ExamsIO constructs an EXAMS model network. This model network is composed of discrete compartments, each representing a spatial volume in the water body network. For each reach in the water body network, a set of compartments is assigned based

on the water body type. Streams, ponds, and wetlands have a single water column compartment, labeled “littoral.” Lakes and bays have two water column compartments, labeled “epilimnion” and “hypolimnion.” Each reach is also assigned two underlying sediment compartments, labeled “benthic.” Compartment numbers are assigned from the surface downward. A water body network of 2 stream reaches would translate to an EXAMS model network of 6 compartments. The first reach in this example is composed of 3 compartments; the surface water is numbered 1, the surficial sediment is numbered 2, and the underlying sediment is numbered 3. The second reach is also composed of 3 compartments, numbered 4, 5, and 6 for the surface water, the surficial sediment, and the underlying sediment. An alternate water body network with the same two stream reaches receiving flow from a headwaters lake reach would have 10 EXAMS compartments. The stream compartments would be numbered as before. The third (lake) reach would be composed of 4 compartments, numbered 7, 8, 9, and 10 for the epilimnion, hypolimnion, surficial sediment, and underlying sediment. To properly translate reach-specific HWIR data to compartment-specific EXAMS data, three mapping vectors are constructed. ReachSWSeg gives the upper surface water compartment number for each reach. ReachBSeg gives the upper benthic compartment number for each reach. Finally, SegReach gives the reach number for each compartment.

From the HWIR site database, stream reaches are assigned lengths, while wetland, pond, lake, and bay reaches are assigned surface areas. Site-specific reach depths and volumes were not available to the HWIR databases. Instead, depths are assigned to water column and sediment compartments for wetlands, ponds, lakes, and bays based on national distributions. ExamsIO calculates volumes from the site-specific surface areas and these estimated depths. For stream reaches, ExamsIO calculates widths and depths using discharge coefficients based on empirical observations of stream hydrogeometric relationships (Leopold and Maddox, 1953), and then calculates volumes using site-specific reach lengths. The following hydrogeometric power functions are used to derive channel width and depth from streamflow:

$$W_{r,t} = a_{hyd_w} @ Q_{r,t}^{b_{hyd_w}} \quad (1)$$

$$d_{r,t} = a_{hyd_d} @ Q_{r,t}^{b_{hyd_d}} \quad (2)$$

where $W_{r,t}$ is stream width for reach r in year t , in m, $d_{r,t}$ is stream depth for reach r in year t , in m, $Q_{r,t}$ is stream flow for reach r in year t , in m^3/sec , and a_{hyd_w} , a_{hyd_d} , b_{hyd_w} , and b_{hyd_d} are hydraulic coefficients. For exact rectangular channels, b_{hyd_d} is 0.6, and b_{hyd_w} is 0. These coefficients are assigned to each stream reach based on a national distribution. Leopold et al. (1964) have noted that stream channels in humid regions tend towards a rectangular cross-section because cohesive soils promote steep side slopes whereas noncohesive soils encourage shallow sloped, almost undefined banks. From a sample of 157 U.S. rivers, they report average values for b_{hyd_d} and b_{hyd_w} .

of 0.45 and 0.12, respectively. For western ephemeral streams, values for $bhyd_d$ and $bhyd_w$ of 0.36 and 0.29 were recommended.

2.2 Water Balance

H-Exams conducts a water balance for each simulated year, routing incoming flows from the headwaters reaches down through the network and out of the exiting reach. For a given reach in a given year, the outflow is the sum of all the inflows minus evaporation:

$$QO_{r,t} = \sum_{j=1}^{WBNRchNumRch_r} QU_{WBNRchRchIndex_{r,j},t} @ WBNRchRchFrac_{r,j} - QS_r - QSeep_r - QR_{r,t} - (R_t \& E_t) @ AS_{r,B} / (100 @ 365) \quad (3)$$

where QO is the average outflow from reach r during year t , in m^3/day , $WBNRchNumRch_r$ is the number of upstream reaches flowing into reach r , $WBNRchRchIndex_{r,i}$ are the upstream reach numbers, QU are the average internal upstream inflows to reach r during year t , in m^3/day , QS is the average external upstream inflow to reach r , in m^3/day , $QSeep$ is the average seepage flow to reach r , in m^3/day , QR is the runoff to reach r during year t , in m^3/day , R is the precipitation for year t , in cm/yr , E is the evaporation for year t , in cm/yr , and AS is the surface area for reach r under baseflow conditions, in m^2 . ExamsIO checks and ensures positive flow in every reach for every year. If evaporation exceeds the total inflow to a reach for a year, ExamsIO reduces evaporation in that reach to a level supporting an outflow of 0.5 mm/year:

$$QO_{r,t} = 0.5 @ AS_{r,B} / (1000 @ 365) \quad (4)$$

Long-term average baseflow from each watershed subbasin is calculated in the HWIR watershed module using empirical correlations with watershed surface area. These flows are mapped to the appropriate reaches using the matrix $WBNRchWSSubIndex_{r,k}$, which gives the k th watershed subbasin number associated with reach r . Total reach baseflow is calculated by summing over all contributing watershed subbasins:

$$QB_r = \sum_{k=1}^{WBNRchNumWSSub_r} BFann_{WBNRchWSSubIndex_{r,k}} @ WBNRchWSSubFrac_{r,k} \quad (5)$$

where QB_r is the baseflow for reach r , in m^3/day , $WBNRchNumWSSub_r$ is the number of watershed subbasins contributing to the baseflow of reach r , $BFann$ is the baseflow contribution

from subbasin number $WBNRchWSSubIndex_{r,k}$ to reach r , in m^3/day , and $WBNRchWSSubFrac_{r,k}$ is the fraction of subbasin $WBNRchWSSubIndex_{r,k}$ that contributes to reach r . This baseflow estimate is derived from observed stream flow data, and accounts for both seepage inflow and evaporation loss during dry periods of time. ExamsIO calculates seepage inflow by adding evaporative loss to baseflow:

$$Q_{Seep_r} = Q_{B_r} + \bar{E} @ AS'_{r,B} / (100 @ 365) \quad (6)$$

where \bar{E} is the average evaporation rate, in cm/yr , and $AS'_{r,B}$ is the surface area of the stream reach (or equivalent stream reach) under baseflow conditions. Even if the reach is a pond, wetland, or lake, the surface area used for this adjustment is calculated as if the reach were a stream (because the HWIR regressions were calculated for baseflow in stream reaches).

Runoff flows for each year t are calculated in a similar manner:

$$QR_{r,t} = \sum_{k=1}^{WBNRchNumWSSub_r} RunoffR_{WBNRchWSSubIndex_{r,k},t} @ WBNRchWSSubFrac_{r,k} \quad (7)$$

where $QR_{r,t}$ is the annual-average runoff flow for reach r in year t , in m^3/day , and $RunoffR$ is the annual-average runoff flow from subbasin number $WBNRchWSSubIndex_{r,k}$ to reach r in year t , in m^3/day .

This water balance is conducted for each simulated year on a reach-specific basis by ExamsIO. The resulting internal flows are used by ExamsIO to calculate stream hydrogeometry and the water body solids balance. ExamsIO passes stream widths and depths and all hydrologic inflows to EXAMS via the batch run file. EXAMS uses this information to recalculate the water balance on a compartment-specific basis for use in its chemical advection calculations.

2.3 Solids Balance

H-Exams conducts a solids balance for each simulated year, routing incoming solids from the headwaters reaches down through the network and out of the exiting reach. The total suspended solids (TSS) in a reach may originate in erosion from adjacent watershed subbasins, from internal bank erosion, or from internal production of biotic solids. Solids deposition and burial is not simulated in this initial version. TSS, then, is modeled as a conservative substance. For a given reach in a given year, the average solids flow through a reach is the sum of all the inflows minus outflows:

$$\begin{aligned}
 & \sum_{j=1}^{WBNRchNumRch_r} QU_{WBNRchRchIndex_{r,j,t}} @ TSS_{WBNRchRchIndex_{r,j,t}} @ WBNRchRchFrac_{r,j} \\
 & \% \sum_{k=1}^{WBNRchNumWSSub_r} SWLoadSolidR_{WBNRchWSSubIndex_{r,k,t}} @ WBNRchWSSubFrac_{r,k} \\
 & \% QO_{r,t} @ SolBnk_r \% QO_{r,t} @ PhytBioMassC(TrophicIndex_r) / WBNfocBioS
 \end{aligned} \tag{8}$$

accounts for watershed erosion loads, where SWLoadSolidR is the solids erosion delivered from The first right-hand term in this equation accounts for upstream solids loads. The second term watershed subbasin WBNRchWSSubIndex_{r,k} during year *t*, in g/day. This erosion load is generated by the HWIR watershed module, and already incorporates an area-dependent sediment delivery ratio. The third term accounts for bank erosion loading, where SolBnk_r is the resulting incremental concentration in reach *r*, in mg/L. SolBnk is set to 5 mg/L for stream reaches, and 1 mg/L otherwise. The final term accounts for internal biotic production of solids, where TrophicIndex_r is the trophic index for reach *r*, PhytBioMassC is the resulting biotic carbon concentration, in mg-C/L, and WBNfocBioS is the organic carbon fraction of biotic solids, in mg-C/mg-solids. The trophic index is related to the net biotic production, as summarized in the table below (Wetzel, 1983):

Trophic Index	1	2	3	4	5	6	7
Trophic Status	ultra-oligo-trophic	oligo-trophic	meso-oligo-trophic	meso-trophic	meso-eutrophic	eutrophic	ultra-eutrophic
Biotic Carbon, mg/L	0.025	0.06	0.10	0.15	0.30	0.50	1.00

These solids calculations are conducted for each simulated year on a reach-specific basis by ExamsIO. The resulting water column TSS concentrations are assigned to each water column compartment and passed to EXAMS via the batch run file.

It should be noted that while EXAMS does not simulate solids movement explicitly, the exchange of sorbed chemical between the water column and the underlying sediment layer is parameterized into a solids dispersion term. This term, described in Section 2.4.4 below, represents such processes as bioturbation and resuspension/resettling.

In shallow upstream reaches that receive large erosion loadings, calculated TSS concentrations can become unreasonably high. This usually occurs during years when evaporation exceeds inflow, causing the reach to concentrate the loadings. The planned addition of deposition and burial processes in later versions of H-Exams should rectify this occasional problem. Meanwhile, in this initial version of H-Exams, a maximum TSS concentration of 10,000 mg/L is imposed. If the calculated TSS concentration in a reach exceeds 10,000 mg/L, then the concentration is reset to this maximum. Resetting the TSS concentration does not affect the chemical mass balance; total chemical concentrations reequilibrate among the dissolved, DOC, and solids phases each time step, as discussed in section 2.4.2 below.

2.4 Chemical Transport and Fate

Chemical fate is calculated entirely within EXAMS on a compartment-specific basis using information supplied by ExamsIO. Chemical fate, represented by temporally- and spatially-variable concentrations, is determined by a set of transport and transformation processes applied within a mass balance framework. EXAMS is based on a series of mass balances, which give rise to a single differential equation for each compartment. Working from the transport and transformation process equations, EXAMS compiles an equation for the net rate of change of chemical concentration in each compartment. The resulting system of differential equations describes a mass balance for the entire aquatic ecosystem. These equations have the following general form:

$$V \frac{dC}{dt} = L_e - L_i - V \cdot K \cdot C \quad (9)$$

where V is the volume of water in the compartment, in m^3 , C is the total chemical concentration as mg/L of V , L_e is the total external loading on the compartment, in g/hr, L_i is the total internal loading on the compartment resulting from contaminated flows among system compartments and the formation of chemical reaction products, in g/hr, and K is an overall pseudo-first-order loss constant that expresses the combined effect of transport and transformation processes that decrease chemical concentration, in hr^{-1} .

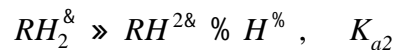
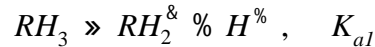
EXAMS handles two kinds of equilibrium processes – ionization and sorption – as well as transport by advection and dispersion, transfer to the atmosphere by volatilization, transformation by several chemical and microbiological processes, and loading through several pathways. Implementation of these processes in H-Exams is discussed in the sections below.

2.4.1 Ionization

Chemicals that ionize exist in two or more species that can exhibit different sorption and transformation properties. H-Exams treats ionization explicitly in order to calculate the neutral

species concentration that is available for volatilization loss. ExamsIO passes values of 0 or 1 for the ionic species flags in EXAMS, so that a chemical is represented as the neutral species plus any appropriate ionic species. For each ionic chemical, a set of temperature-adjusted acid or base dissociation constants are passed to Exams, which then calculates the extent of ionization in each compartment based on water body pH.

Speciation of organic acids – Organic acids donate protons to form negative molecules:



where K_{a1} is the first dissociation constant, given by:

$$K_{a1} = \frac{[H^{\%}] [RH_2^{\&}]}{[RH_3]} \quad (10)$$

and K_{a2} is the second dissociation constant, given by:

$$K_{a2} = \frac{[H^{\%}] [RH^{2\&}]}{[RH_2^{\&}]} \quad (11)$$

Eq. (10) can be rearranged to give the ratio of the neutral to monoanion species:

$$[RH_3] / [RH_2^{\&}] = [H^{\%}] / K_{a1} = 10^{pK_{a1} - pH} \quad (12)$$

where pK_{a1} is the negative base 10 logarithm of the dissociation constant K_{a1} . Likewise, Eq. (11) can be rearranged to give the ratio of the monoanion to the dianion species:

$$[RH_2^{\&}] / [RH^{2\&}] = [H^{\%}] / K_{a2} = 10^{pK_{a2} - pH} \quad (13)$$

where pK_{a2} is the negative base 10 logarithm of the dissociation constant K_{a2} . These equations can be combined to give the fractions in the neutral, monoanion, and dianion species:

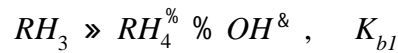
$$f_n = \frac{1}{1 + 10^{pH + pKa1} + 10^{2pH + pKa1 + pKa2}} \quad (14)$$

$$f_{1-} = \frac{10^{pH + pKa1}}{1 + 10^{pH + pKa1} + 10^{2pH + pKa1 + pKa2}} \quad (15)$$

$$f_{2-} = \frac{10^{2pH + pKa1 + pKa2}}{1 + 10^{pH + pKa1} + 10^{2pH + pKa1 + pKa2}} \quad (16)$$

where f_n is the neutral fraction, f_{1-} is the monoanionic fraction, f_{2-} is the dianionic fraction, $pKa1$ is the negative log of the first acid dissociation constant, and $pKa2$ is the negative log of the second acid dissociation constant.

Speciation of organic bases – Organic bases accept protons to form positive molecules:



where K_{b1} is the first dissociation constant, given by:

$$K_{b1} = \frac{[OH^-] [RH_4^+]}{[RH_3]} \quad (17)$$

and K_{b2} is the second dissociation constant, given by:

$$K_{b2} = \frac{[OH^-] [RH_5^{2+}]}{[RH_4^+]} \quad (18)$$

Eq. (17) can be rearranged to give the ratio of the neutral to monocation species:

$$[RH_3] / [RH_4^+] = [OH^-] / K_{b1} = 10^{pK_{b1} + pOH} = 10^{pK_{b1} + pK_w - pH} \quad (19)$$

where pK_{b1} is the negative base 10 logarithm of the dissociation constant K_{b1} , and pK_w is the negative base 10 logarithm of the dissociation constant for water, which is close to 14. Likewise, Eq. (18) can be rearranged to give the ratio of the monocation to the dication species:

$$\frac{[RH_4^+]}{[RH_5^{2+}]} = \frac{[OH^-]}{K_{b2}} \cdot 10^{pK_{b2} + pOH} = 10^{pK_{b2} + pK_w - pH} \quad (20)$$

where pK_{b2} is the negative base 10 logarithm of the dissociation constant K_{b2} . These equations can be combined to give the fractions in the neutral, monocation, and dication species:

$$f_n = \frac{1}{1 + 10^{pK_w + pH + pK_{b1}} + 10^{2pK_w + 2pH + pK_{a1} + pK_{a2}}} \quad (21)$$

$$f_{1+} = \frac{10^{pK_w + pH + pK_{b1}}}{1 + 10^{pK_w + pH + pK_{b1}} + 10^{2pK_w + 2pH + pK_{a1} + pK_{a2}}} \quad (22)$$

$$f_{2+} = \frac{10^{2pK_w + 2pH + pK_{a1} + pK_{a2}}}{1 + 10^{pK_w + pH + pK_{b1}} + 10^{2pK_w + 2pH + pK_{a1} + pK_{a2}}} \quad (23)$$

where f_n is the neutral fraction, f_{1+} is the monocationic fraction, f_{2+} is the dicationic fraction, and pK_a is the negative log of the acid dissociation constant.

Effect of speciation on other reactions – Separate rate constants and partition coefficients are not passed to EXAMS for each ionic species. Rather, the effects of ionization on these properties are handled implicitly. The extent of ionization of a chemical is calculated in the HWIR chemical processor based on the water body temperature and pH, and the lumped chemical properties are adjusted accordingly. For example, the lumped partition coefficient provided by the chemical processor is the weighted mean:

$$K_{oc} = f_n \cdot K_{oc,n} + \sum_i f_i \cdot K_{oc,i} \quad (24)$$

where K_{oc} is the lumped organic carbon partition coefficient, in L/kg, $K_{oc,n}$ is the neutral organic carbon partition coefficient, in L/kg, f_i is the fraction of the chemical in ionic species “i,” and $K_{oc,i}$ is the ionic organic carbon partition coefficient, in L/kg. If the partition coefficient is 100 for the neutral species and 1000 for the cation, then the lumped partition coefficient read by ExamsIO and provided to EXAMS would be 550. EXAMS then applies the lumped coefficients to all ionic species being simulated. Because partitioning is linear, this yields the same total sorbed and neutral fractions as if the separate neutral and ionic partition coefficients had been used explicitly by EXAMS. This implicit procedure would yield errors if different transformation rate constants are applied to the ionic and neutral sorbed chemical phases. While differences in species-phase reactivity is allowed by EXAMS, this capability is not used in this HWIR implementation.

The HWIR chemical processor calculates ionic partition coefficients as the product of the neutral partition coefficient and a multiplication factor. This factor is set to 10^{-4} for dianions, 10^{-2} for monoanions, 10 for monocations, and 10^2 for dications.

2.4.2 Sorption

H-Exams does treat sorption to solids and biota, and complexation to DOC explicitly. These processes are represented as linear equilibrium reactions and are represented by appropriate partition coefficients:

$$C_S = K_{PS} @ C_W \quad (25)$$

$$C_B = K_{PB} @ C_W \quad (26)$$

$$C_{DOC} = K_{DOC} @ C_W \quad (27)$$

where C_W is the dissolved chemical concentration, mg/L-water, C_S is the chemical concentration sorbed to solids, mg/kg-solids, C_B is the chemical concentration taken up into biota, mg/kg-biota, C_{DOC} is the chemical concentration complexed with dissolved organic carbon, mg/kg-DOC, K_{PS} is the partition coefficient that relates the sorbed concentration to the dissolved concentration, (mg/kg-solids)/(mg/L-water), K_{PB} is the partition coefficient that relates the biosorbed concentration to the dissolved concentration, (mg/kg-biota)/(mg/L-water), K_{DOC} is the partition coefficient that relates the DOC-complexed concentration to the dissolved concentration, (mg/kg-DOC)/(mg/L-water), and DOC is the dissolved organic carbon concentration, mg/L-water. . The volumetric concentration of DOC-bound chemical is related to the amount of DOC present:

$$C_{DOC} = K_{DOC} @ C_W @ (DOC @ 10^{&6}) \quad (28)$$

where C_{DOC} is the DOC-complexed concentration in mg/L. The partition coefficients are estimated in different ways for organic chemicals and heavy metals, as summarized in the following sections.

Organic chemicals – For organic chemicals, the organic carbon partition coefficient K_{OC} is used along with the organic carbon fraction of solids f_{OC} to calculate the effective partition coefficient to solids K_{PS} :

$$K_{PS} = K_{OC} \cdot f_{OC} \quad (29)$$

where K_{OC} has units of (mg/kg-organic C)/(mg/L-water) and f_{OC} is the organic carbon content of the solids, expressed as a unitless fraction. For organic chemicals, ExamsIO simply passes the value of K_{OC} from the HWIR chemical SSF to the Exams chemical input file, and the values of f_{OC} for suspended and benthic sediments from the HWIR site SSF to the EXAMS environment input file. EXAMS internally calculates partition coefficients for biotic solids and for DOC based on the following empirical equations:

$$K_{PB} = 0.436 \cdot K_{OW}^{0.907} \quad (30)$$

$$K_{DOC} = 0.020 \cdot K_{OW} \quad (31)$$

where K_{OW} is the octanol-water partition coefficient, in (mg/L-octanol)/(mg/L-water). Computation of K_{PB} from K_{OW} is from Baughman and Paris (1981). The computation of K_{DOC} as 2% of K_{OW} is based on a regression analysis of data in Chiou et al. (1986) and Servos et al. (1989).

Heavy metals – H-Exams employs a different technique for the sorption of inorganic chemicals and metals, which are classified as type “M” and “Hg” in the HWIR chemical SSF. As an organic chemical fate model, EXAMS contains no algorithms for the sorption of metals. Instead, distributions of effective partition coefficients for inorganics and metals to benthic sediments and suspended solids were compiled by Allison et al. (U.S. EPA, 1999) and are incorporated into the HWIR chemical database. These partition coefficients are represented here as K_{PBS} and K_{PSS} for benthic sediment and for suspended solids, in (mg/kg-solids)/(mg/L-water). For each simulation, specific values for K_{PBS} and K_{PSS} are placed into the chemical SSF. ExamsIO transfers this information to EXAMS by making the following assignments:

$$K_{OC} = K_{PSS} \quad (32)$$

$$f_{OC}(\text{water column}) = 1.0 \quad (33)$$

$$f_{OC}(\text{benthic sediment}) = K_{PBS} / K_{PSS} \quad (34)$$

Thus, when EXAMS internally calculates K_{PS} as the product of K_{OC} and f_{OC} for type “M” and “Hg” chemicals, it correctly arrives at K_{PSS} for water column compartments and K_{PBS} for benthic compartments.

For uptake of metals into benthic biota, K_B is set equal to the bioaccumulation factor for benthic filter feeders (variable ChemBenthffBAFm in the chemical database, in L/kg-benthos). For complexation of metals with DOC, K_{DOC} is set to K_{OC} . There is little data on metals-DOC partitioning reported in the scientific literature (U.S. EPA, 1999). The initial HWIR software package omits metals-DOC complexation by setting K_{OC} to 0 for metals and inorganic chemicals.

2.4.3 Advection

EXAMS includes a simple calculation of steady-state average transport of water throughout the computational network. The flow of water acts as a direct carrier of dissolved chemical between two compartments:

$$L_{D\text{adv},j,i} = QO_j \cdot f_{\text{adv},j,i} \cdot C_{Dj} \quad (35)$$

where $L_{D\text{adv},j,i}$ is the dissolved chemical load advected from compartment j to compartment i , in g/hr, QO_j is the net advective outflow from compartment j , in m^3/hr , $f_{\text{adv},j,i}$ is the advection parameter, which gives the fraction of outflow from compartment j that is advected to compartment i , and C_{Dj} is the dissolved chemical concentration in compartment j , in mg/L. In addition, the flow of water between water column compartments carries solids and sorbed chemical downstream:

$$L_{S\text{adv},j,i} = QO_j \cdot f_{\text{adv},j,i} \cdot (S_j C_{Sj} + B_j C_{Bj}) \quad (36)$$

where $L_{S\text{adv},j,i}$ is the total sorbed chemical load (sediment plus biota) advected from compartment j to compartment i , in g/hr, S_j is the sediment solids concentration in compartment j , in kg/L, B_j is the biotic solids concentration in compartment j , in kg/L, C_{Sj} is the sorbed chemical concentration in compartment j , in mg/kg, and C_{Bj} is the biosorbed chemical concentration in compartment j , in mg/kg. EXAMS implements these equations using a set of advection pathways specified in the batch input files. Each pathway connects two compartments, and is defined by three variables: the exporting compartment JFRADG, the importing compartment ITOADG, and the advection parameter ADVPRG.

The EXAMS hydrologic subroutine operates on three subsets of the environmental database. The first subset is a description of the flows entering (or leaving) each compartment from external

sources, including upstream inflow, groundwater inflow (baseflow), overland runoff, rainfall, and evaporation. The second data subset categorizes the geometry of the system, and the properties and distribution of biomass and sediments. The third subset contains structural properties of the ecosystem itself. This specifies the direction and strength of flow pathways interconnecting the system compartments. The flow of water through the system compartments is computed from a mass balance on water entering and leaving each compartment. Since the volume of each compartment is a constant specified value, the hydrologic inputs to a compartment are balanced by advected flows leaving the compartment. H-Exams does provide for stream compartment volumes that vary annually with stream flow. This is accomplished by calculating the yearly-average flows by reach in ExamsIO, then applying the hydraulic geometry equations (1) and (2) to stream reaches and storing the updated widths and depths in the EXAMS run file along with the updated hydrologic inflows. EXAMS then solves the flow balance internally and transports contaminant masses across compartment boundaries throughout the network.

In H-Exams, external stream inflows can be specified by reach but are constant in time. These flows enter the water column compartment directly, bringing in constant upstream chemical and solids loadings. In a similar manner, seepage flows vary by reach but are constant in time. In each reach, seepage flow enters the underlying benthic compartment, bringing in a time-variable chemical loading from one contaminated groundwater plume. These flows are directed upward through the surficial benthic compartment into the water column compartment carrying dissolved chemical concentrations. Overland runoff flows vary by reach and by time. In each reach, runoff flow enters the upper surface water compartment, bringing in time-variable chemical and solids loadings from adjacent watershed subbasins. Rainfall varies by time, adding flows to surface water compartments proportional to their surface areas. Rainfall carries in atmospheric wetfall loadings that are time-variable. Finally, evaporation varies by reach and by time, subtracting flows from surface water compartments that are proportional to their surface areas. Chemical and solids are, of course, not removed by evaporation flows.

2.4.4 Dispersion

In addition to the mean advected flow, water is transported throughout an aquatic system by a series of mixing processes that are conventionally lumped together and described as dispersion. EXAMS calculates these dispersive water flows in a conventional manner:

$$QR_{i,j} = n_{i,j} \frac{E_{i,j} @ AS_{i,j}}{LC_{i,j}} \quad (37)$$

where $QR_{i,j}$ is the exchange flow between compartments i and j , in m^3/hr , $n_{i,j}$ is the characteristic porosity of compartments i and j , in L_{water}/L (equal to 1.0 for exchange between two surface water compartments, the arithmetic average porosity for exchange between two benthic compartments,

and the benthic porosity for exchange between benthic and water column compartments), $E_{i,j}$ is the dispersive exchange coefficient, in m^2/hr , AS_{ij} is the surface area through which exchange takes place, in m^2 , and LC_{ij} is the characteristic mixing length over which exchange takes place, in m . This exchange flow acts as a direct carrier of dissolved chemical between two compartments, as implemented by EXAMS in a pair of equations:

$$L_{D\ disp\ j,i} = QR_{ij} @ C_{Dj} \quad ; \quad L_{D\ disp\ i,j} = QR_{ij} @ C_{Di} \quad (38)$$

where $L_{D\ disp\ j,i}$ is the dissolved chemical load transported from compartment j to compartment i , in g/hr , $L_{D\ disp\ i,j}$ is the dissolved chemical load transported from compartment i to compartment j , in g/hr , C_{Dj} is the dissolved chemical concentration in compartment j , in mg/L , and C_{Di} is the dissolved chemical concentration in compartment i , in mg/L . In addition, the exchange of water between water column compartments mixes solids and sorbed chemical, as implemented by EXAMS in a pair of equations:

$$L_{S\ disp\ j,i} = QR_{ij} @ (S_j C_{Sj} \% B_j C_{Bj}) \quad ; \quad L_{S\ disp\ i,j} = QR_{ij} @ (S_i C_{Si} \% B_i C_{Bi}) \quad (39)$$

where $L_{S\ disp\ j,i}$ is the total sorbed chemical load (sediment plus biota) mixed from compartment j to compartment i , in g/hr , and $L_{S\ disp\ i,j}$ is the total sorbed chemical load (sediment plus biota) mixed from compartment i to compartment j , in g/hr . When exchange occurs between water column and benthic compartments, the dissolved chemical exchange loads are as described above. In this case, however, the solids themselves are assumed not to exchange between benthic and water column compartments. Rather, a fraction of the benthic solids are temporarily mixed into the water column, chemical is equilibrated between these solids and the water column, and the solids are returned to the benthic layer. The amount of sorbed water column chemical captured by the mixing bed solids is proportional to the relative sorption capacities of the benthic and water column solids. For exchange between benthic compartment j and water column compartment i :

$$L_{S\ disp\ j,i} = \left(\frac{QR_{ij} @ S_j}{n_j} \right) @ C_{Sj} \quad ; \quad L_{S\ disp\ i,j} = \left(\frac{QR_{ij} @ S_j}{n_j} \right) @ C_{Si} @ \frac{K_{Pj}}{K_{Pi}} \quad (40)$$

where K_{Pj} is the partition coefficient for solids in benthic compartment j , in L_w/kg_s , and K_{Pi} is the partition coefficient for solids in water column compartment i , in L_w/kg_s . The term in parentheses is the temporary sediment flux exchanging with the water column in Mg/hr , and is assumed to be proportional to the benthic-water column dispersive flow.

EXAMS implements these equations using a set of dispersion pathways specified in the batch input files. Each pathway connects two compartments, and is defined by five variables: the

exchange compartments JTURBG and ITURBG, the cross-sectional surface area XSTURG, the characteristic mixing length CHARLG, and the dispersion coefficient DSPG..

H-Exams provides for dispersive exchange vertically within a reach, but not horizontally between reaches. Values for sediment-water column dispersion coefficient are provided by water body type (stream, lake/pond/bay, and wetland). In addition, a dispersion coefficient for exchange across the thermocline is provided.

2.4.5 Volatilization

The dissolved, neutral species of a chemical may escape from surface water compartments to the atmosphere through volatilization. EXAMS treats volatilization as a first-order loss process. The loss rate constant applied to the total chemical concentration is given by:

$$k_{v,i} = \frac{K_{v,i} \cdot f_{dn,i} \cdot AS_i}{V_i} \quad (41)$$

where $k_{v,i}$ is the volatilization loss rate constant from compartment i , in hr^{-1} , $K_{v,i}$ is the overall transfer rate, or conductivity from compartment i , in m/hr , AS_i is the surface area of compartment i , in m^2 , V_i is the volume of compartment i , in m^3 , and $f_{dn,i}$ is the dissolved, neutral fraction of chemical in compartment i .

The conductivity is determined by the two-layer resistance model (Whitman, 1923; or see Burns, et al., 1982). The two-layer resistance method assumes that two "stagnant films" are bounded on either side by well mixed compartments. Concentration differences serve as the driving force for the water layer diffusion. Pressure differences drive the diffusion for the air layer. Mass balance requires that the same flux must pass through both films; thus, the two resistances combine in series, so that the conductivity is the reciprocal of the total resistance:

$$K_{v,i} = (R_{L,i} \cdot R_{G,i})^{-1} \cdot \left(K_{L,i}^{-1} \cdot \left(K_{G,i} \cdot \frac{H}{R \cdot T_K} \right)^{-1} \right)^{-1} \quad (42)$$

where $R_{L,i}$ is the liquid phase resistance, in hr/m , $K_{L,i}$ is the liquid phase transfer coefficient, in m/hr , $R_{G,i}$ is the gas phase resistance, in hr/m , $K_{G,i}$ is the gas phase transfer coefficient, in m/hr , R is the universal gas constant, $8.206 \times 10^{-5} \text{ atm} \cdot \text{m}^3/\text{mole} \cdot \text{K}$, H is the Henry's law constant, in $\text{atm} \cdot \text{m}^3/\text{mole}$, and T_K is the water body temperature, in K .

Following a suggestion by Liss and Slayter (1974), EXAMS indexes the phase transfer conductivities of chemical pollutants against the exchange properties of well-studied environmental

substances -- water and oxygen. Water itself has no transport resistance in the liquid phase of the interface: its transport is controlled by events in the atmospheric zone of the interface, and so is used to compute chemical gas phase conductivity:

$$K_{G,i} = K_{Wat,i} @ \sqrt{18/MW} \quad (43)$$

where $K_{Wat,i}$ is the water vapor exchange constant, in m/hr, 18 is the molecular weight of water, and MW is the molecular weight of the volatilizing chemical. The water vapor exchange constant is calculated in EXAMS as a function of wind speed based on Liss (1973):

$$K_{Wat,i} = 0.1857 + 11.36 @ W_{0.1} \quad (44)$$

where $W_{0.1}$ is the wind speed 0.1 meters above the water surface, in m/sec (the empirical equation adjusts for the change in units). Observed wind speed from meteorological stations at a height of 6 meters can be multiplied by 0.53 to obtain expected wind speed at 0.1 meter assuming a logarithmic velocity profile and an effective roughness height of 1 mm (Burns et al., 1982). Meteorological stations vary in height, with a median near 18 feet. A constant multiplication factor of 0.5 was used to correct wind speed from meteorological stations to wind speed at 0.1 meters.

The transport of oxygen across the air-water interface of aquatic systems (reaeration) is controlled by resistance in the liquid phase (Liss, 1973), and is used by EXAMS to compute chemical liquid phase conductivity:

$$K_{L,i} = K_{O_2} @ \sqrt{32/MW} \quad (45)$$

where K_{O_2} is the reaeration constant, in m/hr and 32 is the molecular weight of oxygen. Values for K_{O_2} are calculated in ExamsIO by reach and are transferred to EXAMS (using the proper EXAMS input units of cm/hr) in the environment and batch run files. Different methods are used to calculate reaeration for flowing systems (streams) and stagnant systems (ponds, wetlands, lakes, and bays).

ExamsIO calculates flow-induced reaeration based on the Covar method (Covar, 1976; summarized in Bowie, et al., 1985). This method calculates reaeration as a function of velocity and depth by one of three formulas -- Owens, Churchill, or O'Connor- Dobbins, respectively:

$$k_{qi}(20EC) = \frac{5.349}{24} @ \frac{v_i^{0.67}}{z_i^{0.85}} \quad (46)$$

$$k_{qi}(20EC) = \frac{5.049}{24} @ \frac{v_i^{0.97}}{z_i^{0.673}} \quad (47)$$

or

$$k_{qi}(20EC) = \frac{3.93}{24} @ \frac{v_i^{0.50}}{z_i^{0.50}} \quad (48)$$

where k_{qi} is the flow-induced reaeration rate coefficient at 20EC, in m/hr, v_i is the average water velocity in compartment i , in m/sec, and z_i is the average compartment i depth, in m.

The Owens formula is automatically selected for compartments with depth less than 2 feet. For compartments deeper than 2 feet, the O'Connor-Dobbins or Churchill formula is selected based on a consideration of depth and velocity. Deeper, slowly moving rivers require O'Connor-Dobbins; moderately shallow, faster moving streams require Churchill. Rivers over 2 feet deep with velocities less than 1.7 feet/second always use O'Connor-Dobbins. Segment temperatures are used to adjust the flow-induced $k_{qi}(20 EC)$ by the standard formula:

$$K_{O_2} = k_{qi}(20EC) T_a^{T&20} \quad (49)$$

where T is the water temperature, in EC, K_{O_2} is the reaeration rate coefficient at ambient segment temperature, in m/hr, and T_a is the temperature coefficient, set to 1.026.

Wind-induced reaeration is determined by O'Connor (1983). This method calculates reaeration as a function of wind speed, air and water temperature, and depth using one of three formulas:

$$K_{O_2} = \frac{3600}{100} \left(\frac{D_{OW}}{\rho_w} \right)^{2/3} \left(\frac{\rho_a}{\rho_w} \right)^{1/2} \frac{\nu_a^{1/3}}{G} \sqrt{C_d} (100 W_{10}) \quad (50)$$

$$K_{O_2} = \frac{3600}{100} \left[(TERM1 @ 100 W_{10})^{0.1} + (TERM2 \sqrt{100 W_{10}})^{0.1} \right]^{0.1}$$

where

$$TERM1 = \left(\frac{D_{OW}}{\rho_w} \right)^{2/3} \left(\frac{\rho_a}{\rho_w} \right)^{1/2} \frac{\nu_a^{1/3}}{G_u} \sqrt{C_d} \quad (51)$$

$$TERM2 = \left(\frac{D_{OW}}{\rho_{z_0}} \frac{\rho_a \nu_a}{\rho_w \nu_w} \sqrt{C_d} \right)^{1/2}$$

or

$$K_{O_2} = \frac{3600}{100} \left(\frac{D_{OW}}{\rho_{z_e}} \frac{\rho_a \nu_a}{\rho_w \nu_w} \sqrt{C_d} \right)^{1/2} \sqrt{100 W_{10}} \quad (52)$$

where K_{O_2} is the wind-induced reaeration rate coefficient, in m/hr, W_{10} is time-varying wind speed at 10 m above surface, in m/sec, T_a is air temperature, in EC, ρ_a is the density of air, a function of T_a , in g/cm³, ρ_w is the density of water, 1.0 g/cm³, ν_a is the viscosity of air, a function of T_a , in cm²/s, ν_w is the viscosity of water, a function of T , in cm²/s, D_{OW} is the diffusivity of oxygen in water, a function of T , in cm²/s, κ is von Karman's coefficient, 0.4, v_t is the transitional shear velocity, set to 9, 10, and 10 for small, medium, and large scales, in m/s, v_c is the critical shear velocity, set to 22, 11, and 11 for small, medium, and large scales, in cm/s, z_e is equivalent roughness, set to 0.25, 0.35, and 0.35 for small, medium, and large scales, in cm, z_0 is effective roughness, a function of z_e , G , C_d , ν_a , and $W_{0.1}$, in cm, ν is the inverse of Reynold's number, set to 10, 3, and 3 for small, medium, and large scales, G is the non-dimensional coefficient, set to 10, 6.5, and 5 for small, medium, and large scales, G_u is the non-dimensional coefficient, a function of G , v_c , C_d , and $W_{0.1}$, and C_d is the drag coefficient, a function of z_e , G , ρ_a , ν , v_t , and $W_{0.1}$.

Eq.(50) is used for wind speeds of up to 6 m/sec, where interfacial conditions are smooth and momentum transfer is dominated by viscous forces. Eq.(52) is used for wind speeds over 20 m/sec, where interfacial conditions are rough and momentum transfer is dominated by turbulent eddies. Eq.(51) is used for wind speeds between 6 and 20 m/sec, and represents a transition zone in which the diffusional sublayer decays and the roughness height increases.

Details on the calculation of air density, air and water viscosity, the drag coefficient, the effective roughness, and G_u can be found in O'Connor (1983). Small scale represents laboratory conditions. In this H-Exams application, medium scale is used to represent ponds and wetlands, while large scale represents lakes and bays.

2.4.6 Organic Chemical Transformation Reactions

EXAMS contains process modules for several chemical transformation reactions, including hydrolysis (acid, base, and neutral), biodegradation (water column and sediments), photolysis, oxidation, and reduction. EXAMS uses these modules as determined by the input chemical properties. Each of the unit process equations used to compute the transformation kinetics accounts for the interactions between the chemistry of a compound and the environmental forces that shape its behavior in aquatic systems. In addition, specified reaction pathways account for the production of transformation products of concern, whose further fate and transport can then be simultaneously simulated by EXAMS.

In the H-Exams implementation, the chemical kinetics are calculated by the HWIR chemical processor, and the net first-order transformation rate constants are provided for hydrolysis, aerobic biodegradation, anaerobic biodegradation, and reduction. For each of these reactions the HWIR chemical database also provides information on up to five transformation pathways, including the product name, the product CAS identification number, and the molar reaction yield coefficient. In the first HWIR implementation, the transformation pathways are utilized only in the simulation of mercury.

Hydrolysis – EXAMS calculates hydrolysis transformation rates for the acid-catalyzed pathway, the base-catalyzed pathway, and the neutral pathway using specific rate constants for each ionic species and sorption phase. The overall hydrolysis equation is the following:

$$R_{hydrolysis,i} = V_i \sum_{k=1}^7 C_i \sum_{p=1}^3 \left(kAH_{p,k} [H^+]_i + kNH_{p,k} + kBH_{p,k} [OH^-]_i \right) f_{p,k,i} \quad (53)$$

where $R_{hydrolysis,i}$ is the overall hydrolysis loss rate in compartment i , in g/hr, V_i is the volume of compartment i , in m^3 , C_i is the total chemical concentration in compartment i , in mg/L, k represents the ionic species (0, +1, +2, +3, -1, -2, -3), p represents the sorption phase (dissolved, sediment-

sorbed, DOC-complexed), $kA_{p,k}$ is the acid-catalyzed hydrolysis rate constant for ionic species k phase p , in L/mole-hr, $[H^+]_i$ is the hydrogen ion concentration in compartment i , in mole/L, $kN_{p,k}$ is the neutral hydrolysis rate constant for ionic species k phase p , in hr^{-1} , $kB_{p,k}$ is the base-catalyzed hydrolysis rate constant for ionic species k phase p , in L/mole-hr, $[OH^-]_i$ is the hydroxide ion concentration in compartment i , in mole/L, and $f_{p,k}$ is the fraction of the total chemical concentration in compartment i that is in ionic species k phase p . The entire double summation expression constitutes the overall hydrolysis loss rate constant reflecting the extent of ionization and sorption in each compartment.

H-Exams reads a total hydrolysis rate constant ChemHydRate from the chemical database. This rate constant accounts for the effects of ionization based on an overall water body pH, but not for the effects of sorption. H-Exams assigns ChemHydRate to the EXAMS dissolved phase neutral hydrolysis rate constant $kN_{1,1}$, adjusting units from day^{-1} to hr^{-1} . H-Exams assigns 0 to all other EXAMS hydrolysis rate constants, so that the equation implemented reduces to:

$$R_{hydrolysis} = \sum_i V_i C_i @ kN_{1,1} @ f_{D,i} \quad (54)$$

where $f_{D,i}$ is the fraction of chemical in the dissolved phase in compartment i .

Biodegradation – EXAMS calculates biodegradation transformation rates for water column and for benthic compartments using specific rate constants for each ionic species and sorption phase:

$$R_{bac\ W,i} = \sum_{k=1}^7 \sum_{p=1}^3 V_i C_i @ (kBACW_{p,k} @ [Bac\ W]_i) @ f_{p,k} \quad (55)$$

$$R_{bac\ S,i} = \sum_{k=1}^7 \sum_{p=1}^3 V_i C_i @ \left(kBACS_{p,k} @ \frac{[Bac\ S]_i}{(PCTWA_i \& 100)} \right) @ f_{p,k} \quad (56)$$

where $R_{bac\ W,i}$ and $R_{bac\ S,i}$ are the overall biodegradation loss rates for water column and benthic compartments, in g/hr, V_i is the volume of compartment i , in m^3 , C_i is the total chemical concentration in compartment i , in mg/L, k represents the ionic species, p represents the sorption phase, $kBACW_{p,k}$ is the water column biodegradation rate constant for ionic species k phase p , in mL/cells-hr, $[Bac\ W]_i$ is the active microbial population in water column compartment i , in cells/mL, $kBACS_{p,k}$ is the benthic biodegradation rate constant for ionic species k phase p , in mL/cells-hr, $[Bac\ S]_i$ is the active microbial population in benthic compartment i , in cells/100 g dry weight sediment, $PCTWA_i$ is the “percent water” in benthic segment i , calculated as 100 times the fresh weight (solids plus water) divided by the dry weight of sediment, and $f_{p,k}$ is the fraction of the total chemical concentration in compartment i that is in ionic species k phase p . The term

(PCTWA-100) is 100 times the water volume divided by the sediment mass, and has units of decagrams-solids/mL-water. This term converts the input microbial biomass in cells/100g to the internal unit of cells/mL-water. The entire double summation expressions constitute the overall biodegradation loss rate constants reflecting the extent of ionization and sorption in each compartment.

H-Exams reads the total aerobic and anaerobic biodegradation rate constants, ChemAerBioRate and ChemAnaBioRate, respectively, from the chemical database. H-Exams assigns ChemAerBioRate to the EXAMS dissolved phase neutral water column biodegradation rate constant $kBACW_{1,1}$, adjusting units from day^{-1} to hr^{-1} . Likewise, H-Exams assigns ChemAnaBioRate to the EXAMS dissolved phase neutral benthic biodegradation rate constant $kBACS_{1,1}$, adjusting units from day^{-1} to hr^{-1} . Water column microbial densities are set to 1.0, while benthic microbial densities are set to (PCTWA - 100). H-Exams assigns 0 to all other EXAMS biodegradation rate constants, so that the equations implemented reduce to:

$$R_{Bac W,i} = V_i @ C_i @ kBACW_{1,1} @ f_{D,i} \quad (57)$$

$$R_{Bac S,i} = V_i @ C_i @ kBACS_{1,1} @ f_{D,i} \quad (58)$$

Reduction – EXAMS calculates reductive transformation rates using specific rate constants for each ionic species and sorption phase:

$$R_{reduction,i} = V_i @ C_i @ \sum_{k=1}^7 \sum_{p=1}^3 (kRED_{p,k} @ [Reductant]_i) @ (f_{p,k})_i \quad (59)$$

where $R_{reduction,i}$ is the overall reductive loss rate for compartment i , in g/hr, $kRED_{p,k}$ is the reduction rate constant for ionic species k phase p , in L/mg-reductant-hr, and $[Reductant]_i$ is the reductant concentration in compartment i , in mg/L. The entire double summation expression constitutes the overall reduction loss rate constant reflecting the extent of ionization and sorption in each compartment.

H-Exams reads the total reduction rate constant ChemAnaRedRate from the chemical database and assigns it to the EXAMS dissolved neutral species reduction rate constant $kRED_{1,1}$, adjusting units from day^{-1} to hr^{-1} . Water column reductant concentrations are set to 0, while benthic reductant concentrations are set to 1.0, implementing this reaction in the benthic compartments only. H-Exams assigns 0 to all other EXAMS reduction rate constants, so that the equation implemented reduces to:

$$R_{Reduction} = V_i @ C_i @ kRED_{1,1} @ f_{D,i} \quad (60)$$

2.4.7 Mercury Transformation Reactions

Mercury is simulated in H-Exams with three interacting chemical components representing inorganic divalent mercury (HgII), methyl mercury (MeHg), and elemental mercury (Hg0). Atmospheric and watershed loadings are predominantly in the form of HgII. In the water body, HgII can be reduced to Hg0 and methylated to MeHg. Hg0 can be oxidized back to HgII and volatilized to the atmosphere. MeHg can be demethylated back to HgII and to Hg0.

To implement these mercury reactions, H-Exams sets the number of chemicals to 3, assigning component HgII to chemical 1, MeHg to chemical 2, and Hg0 to chemical 3. The CAS identification numbers, ChemCASID in the chemical database, are set to 7439-97-6 for HgII, 7439-97-6m for MeHg, and 7439-97-6e for Hg0. As an organic chemical model, EXAMS handles volatilization but does not include process modules for the mercury transformation reactions. These are handled by passing appropriate mercury transformation rate constants and yield coefficients to the EXAMS biodegradation and reduction reactions for each mercury component. In order to make EXAMS treat these transformation rate constants as first-order, water column reductant concentrations and microbial densities are set to 1.0, while benthic microbial densities are set to (PCTWA - 100). All transformation pathways are identified by a unique path number, which increments from 1 to the total number of reactions. Rate constants are passed to EXAMS in the chemical files "hwirexp*.chm," while reaction pathways and yields are included in the batch command file "hwirexp.exe."

Methylation – Methylation of dissolved and particulate HgII in the water column are the first two reaction pathways set. H-Exams reads the rate constant ChemAerBioRate(1) from the chemical database, adjusts the units to hr^{-1} , and assigns the value to the EXAMS water column dissolved and particulate biodegradation rate constants $kBACW_{1,1,1}$ and $kBACW_{2,1,1}$. The EXAMS parent compound identifiers CHPAR(1) and CHPAR(2) are set to 1. H-Exams reads the reaction product identification ChemAerBioProdCASID(1) from the chemical database, identifies the product as MeHg, and sets the EXAMS product identifiers TPROD(1) and TPROD(2) to 2. H-Exams transfers the molar yield coefficient ChemAerBioProdYield(1) from the chemical database to EXAMS variables YIELD(1) and YIELD(2).

Methylation of dissolved and particulate HgII in the sediments are the 3rd and 4th reaction pathways set. H-Exams reads the rate constant ChemAnaBioRate(1) from the chemical database, adjusts the units to hr^{-1} , and assigns the value to the EXAMS water column dissolved and particulate biodegradation rate constants $kBACS_{1,1,1}$ and $kBACS_{2,1,1}$. The EXAMS parent compound identifiers CHPAR(3) and CHPAR(4) are set to 1. H-Exams reads the reaction product identification ChemAnaBioProdCASID(1) from the chemical database, identifies the product as MeHg, and sets the EXAMS product identifiers TPROD(3) and TPROD(4) to 2. H-Exams transfers the molar yield

coefficient ChemAnaBioProdYield(1) from the chemical database to EXAMS variables YIELD(3) and YIELD(4).

Reduction – Reduction of dissolved and particulate HgII in the water column are the 5th and 6th reaction pathways set. H-Exams reads the rate constant ChemAnaRedRate(1) from the chemical database, adjusts the units to hr⁻¹, and assigns the value to the EXAMS water column dissolved and particulate reduction constants kRED_{1,1,1} and kRED_{2,1,1}. The EXAMS parent compound identifiers CHPAR(5) and CHPAR(6) are set to 1. H-Exams reads the reaction product identification ChemAnaRedProdCASID(1) from the chemical database, identifies the product as Hg0, and sets the EXAMS product identifiers TPROD(5) and TPROD(6) to 3. H-Exams transfers the molar yield coefficient ChemAnaRedProdYield(1) from the chemical database to EXAMS variables YIELD(5) and YIELD(6).

Demethylation – Demethylation of dissolved and particulate MeHg in the water column are the 7th and 8th reaction pathways set. H-Exams reads the rate constant ChemAerBioRate(2) from the chemical database, adjusts the units to hr⁻¹, and assigns the value to the EXAMS water column dissolved and particulate biodegradation rate constants kBACW_{1,1,2} and kBACW_{2,1,2}. The EXAMS parent compound identifiers CHPAR(7) and CHPAR(8) are set to 2. H-Exams reads the reaction product identification ChemAerBioProdCASID(2) from the chemical database, identifies the product as HgII, and sets the EXAMS product identifiers TPROD(7) and TPROD(8) to 1. H-Exams transfers the molar yield coefficient ChemAerBioProdYield(2) from the chemical database to EXAMS variables YIELD(7) and YIELD(8).

Methylation of dissolved and particulate MeHg in the sediments are the 9th and 10th reaction pathways set. H-Exams reads the rate constant ChemAnaBioRate(2) from the chemical database, adjusts the units to hr⁻¹, and assigns the value to the EXAMS water column dissolved and particulate biodegradation rate constants kBACS_{1,1,2} and kBACS_{2,1,2}. The EXAMS parent compound identifiers CHPAR(9) and CHPAR(10) are set to 2. H-Exams reads the reaction product identification ChemAnaBioProdCASID(2) from the chemical database, identifies the product as HgII, and sets the EXAMS product identifiers TPROD(9) and TPROD(10) to 1. H-Exams transfers the molar yield coefficient ChemAnaBioProdYield(2) from the chemical database to EXAMS variables YIELD(9) and YIELD(10).

Demethylation of dissolved and particulate MeHg in the water column by the *Mer* operon are the 11th and 12th reaction pathways set. H-Exams reads the rate constant ChemAnaRedRate(2) from the chemical database, adjusts the units to hr⁻¹, and assigns the value to the EXAMS water column dissolved and particulate reduction rate constants kRED_{1,1,2} and kRED_{2,1,2}. The EXAMS parent compound identifiers CHPAR(11) and CHPAR(12) are set to 2. H-Exams reads the reaction product identification ChemAnaRedProdCASID(2) from the chemical database, identifies the product as Hg0, and sets the EXAMS product identifiers TPROD(11) and TPROD(12) to 3. H-Exams transfers the molar yield coefficient ChemAnaRedProdYield(2) from the chemical database to EXAMS variables YIELD(11) and YIELD(12).

Oxidation – Oxidation of dissolved and particulate Hg⁰ in the water column are the 13th and 14th reaction pathways set. H-Exams reads the rate constant ChemAnaRedRate(3) from the chemical database, adjusts the units to hr⁻¹, and assigns the value to the EXAMS water column dissolved and particulate reduction constants kRED_{1,1,3} and kRED_{2,1,3}. The EXAMS parent compound identifiers CHPAR(13) and CHPAR(14) are set to 3. H-Exams reads the reaction product identification ChemAnaRedProdCASID(3) from the chemical database, identifies the product as HgII, and sets the EXAMS product identifiers TPROD(13) and TPROD(14) to 1. H-Exams transfers the molar yield coefficient ChemAnaRedProdYield(3) from the chemical database to EXAMS variables YIELD(13) and YIELD(14).

2.4.8 Loading

EXAMS provides input vectors for 5 kinds of loadings to each compartment of the surface water system: point source or stream-borne loadings (STRLD), nonpoint source loadings (NPSLD), contaminated ground water seepage (SEELD), precipitation washout from the atmosphere (PCPLD), and spray drift (or miscellaneous) loadings (DRFLD) (all loadings have units of kg-chemical/hr). These vectors allow for monthly and annual-average loadings to all appropriate compartments. All loadings (except DRFLD) must be associated with an appropriate carrier flow -- STRLD with STRFL, NPSLD with NPSFL, and SEELD with SEEFL. PCPLD is restricted to upper surface water compartments that receive RAIN.

EXAMS evaluates the propriety of loadings entering with carrier flows to prevent conditions outside of its operating range. EXAMS makes no provision for crystallization of the compound from solution, nor for dissolution of a compound from a solid or liquid phase. In addition, reaction nonlinearities potentially present at high chemical concentrations are not incorporated into the code. To make this check, EXAMS calculates the dissolved chemical concentration within each carrier flow, using receiving compartment pH and temperature to account for ionization and using entrained sediment loads to account for sorption. If the dissolved concentration for any of the species is greater than half its solubility, then an error message is generated and the simulation is aborted. After checking the loadings, EXAMS sums all the external loads to a compartment and applies a units conversion from kg/hr to g/hr to obtain the term Le of Eq.(9).

Upstream inflow – In setting up the loadings for each simulation, H-Exams first calculates long-term average upstream loadings by reach using upstream flow and upstream chemical concentration found in the SW*.ssf. These loadings are associated with the appropriate compartments and written to the EXAMS environment file as STRLD. These loadings represent chemical sources from outside the area of interest. In this implementation of HWIR, upstream loadings are assumed to be negligible, and the upstream concentration was set to 0.

Watershed runoff – H-Exams processes each of the annual-average runoff flows and loadings from the various watershed subbasins found in the WS.grf. These variables are associated with the

appropriate water body compartments, summed, and written yearly to the EXAMS batch run file as NPSLD.

Groundwater seepage – H-Exams processes each of the annual-average seepage loadings from the contaminated aquifer found in the AQ.grf. This loading history is associated with the appropriate water body compartment and written to the EXAMS batch run file as SEELD. Because groundwater loadings usually vary slowly over a long period of time, the values are updated infrequently. About 100 discrete loading values are used by the aquifer module to define the entire loading history, which can occur over several centuries.

Atmospheric deposition – H-Exams processes each of the annual-average atmospheric fluxes at various points found in the AR.grf. Several discrete deposition points can be mapped to a single pond, wetland, lake, or bay reach. Each point represents a fraction of the reach surface area, and receives vapor wet deposition, particulate wet deposition, and particulate dry deposition fluxes, in $\text{g}/\text{m}^2\text{-day}$ (values are already normalized to the fraction of the total reach area). ExamsIO sums all three deposition fluxes for all points associated with a reach, multiplies this total flux by the reach surface area, converts units, and writes the total atmospheric loadings to the EXAMS batch run file as PCPLD.

Source runoff – H-Exams processes through the annual-average runoff loadings directly from the waste management unit found in SR.grf. This load is associated with the appropriate water body compartment(s) and written yearly to the EXAMS batch run file as DRFLD.

3.0 SOFTWARE FILES AND VARIABLES

The FRAMES-HWIR system creates a set of system-level files to store variables for use by the various simulation modules. The site simulation files (SSFs) contain chemical and environmental variables that are given appropriate values for each Monte-Carlo iteration of the software. The global results files (GRFs) contain hydrological and chemical variables calculated by the various modules during each Monte-Carlo iteration. In addition, the surface water module creates and uses a set of temporary files to communicate between ExamsIO and EXAMS. These files and variables are summarized in the sections below.

3.1 Site Simulation Files

Three site simulation files are generated for each execution of the surface water module – the site layout file sl.ssf, the chemical property file cpstream.ssf, and the surface water body file(s) sw*.ssf (where * stands for the water body number at a site). These are ASCII, comma-delimited files that are accessed by the module using a specially-provided dynamic link library. Each file has a corresponding data dictionary file in the /SSF/ subdirectory (i.e., sl.dic, cp.dic, and sw.dic). The dictionary files list the variable names along with their dimensions, data type (i.e., character or

“string”, real or “float,” or integer), minimum and maximum values, units, and a brief description. For some arrays, the maximum number of entries are also given.

3.1.1 Variables in the SL.SSF

The site layout SSF contains 206 variables that are relevant to the various modules. The following 35 are used by the surface water module.

"**MetSta**",0,"String",,,,"Met. Station identifier (<MetSta>L.dat, <MetSta>A.dat,<MetSta>M.dat,<MetSta>D.dat,<MetSta>H.dat)"

"**NumWBN**",0,"Integer",1,5,,"Number of waterbody networks"

"**NyrMax**",0,"Integer",1,10000,"years", "Maximum model simulation time"

"**TermFrac**",0,"Float",0,1,"fraction", "Peak output fraction for simulation termination"

"**WBNDOC**",1,"Float",0,50,"mg/L", "DOC of stream, lake, and wetland reaches in waterbody network",[3]

"**WBNfocAbs**",0,"Float",0,0.5,"fraction", "fraction organic carbon of abiotic solids in water column"

"**WBNfocBioS**",0,"Float",0.2,1,"fraction", "fraction organic carbon of biotic solids in water column"

"**WBNfocSed**",1,"Float",0,0.5,"fraction", "fraction organic carbon in sediments of stream, lake, and wetland reaches",[3]

"**WBNId**",1,"Integer",0,100, "Environmental Setting Id for WBN",[NumWBN]

"**WBNNumRch**",1,"Integer",1,50, "Number of reaches for this network",[NumWBN]

"**WBNpH**",1,"Float",4,9, "pH units", "pH of stream, lake, and wetland reaches in the waterbody network",[3]

"**WBNRchAirFrac**",3,"Float",0,1,"fraction", "Fraction of this reach impacted by air point", [NumWBN],[WBNNumRch],[WBNRchNumAir]

"**WBNRchAirIndex**",3,"Integer",1,1000, "Index of air point that impacts this reach", [NumWBN],[WBNNumRch],[WBNRchNumAir]

"**WBNRchAquFrac**",3,"Float",0,1,"fraction","Fraction of this reach impacted by the aquifer", [NumWBN],[WBNNumRch],[WBNRchNumAqu]

"**WBNRchAquIndex**",3,"Integer",0,5,,"Index of aquifer that impacts this reach", [NumWBN], [WBNNumRch],[WBNRchNumAqu]

"**WBNRchArea**",2,"Float",0,1000000000,"m2","reach surface area (nonstream reaches)", [NumWBN],[WBNNumRch]

"**WBNRchBodyType**",2,"String",,,, "Type of waterbody (Stream, Lake, Wetland)", [NumWBN], [WBNNumRch]

"**WBNRchHypoAreaFrac**",2,"Float",0,1,"fraction","fraction of total surface area for hypolimnion", [NumWBN],[WBNNumRch]

"**WBNRchLength**",2,"Float",0,10000,"m","Reach Length", [NumWBN],[WBNNumRch]

"**WBNRchNumAir**",2,"Integer",0,100,,"Number of points that impact this reach", [NumWBN], [WBNNumRch]

"**WBNRchNumAqu**",2,"Integer",0,2,,"Number of aquifer that impact this reach", [NumWBN], [WBNNumRch]

"**WBNRchNumLoc**",2,"Integer",1,1000,"unitless","number of x,y points associated with watershed", [NumWBN],[WBNNumRch]

"**WBNRchNumRch**",2,"Integer",0,50,,"Number of reaches that impact this reach", [NumWBN], [WBNNumRch]

"**WBNRchNumWSSub**",2,"Integer",0,50,,"Number of watersheds that impacts this reach", [NumWBN],[WBNNumRch]

"**WBNRchOrder**",2,"Integer",1,7,"unitless","stream order", [NumWBN],[WBNNumRch]

"**WBNRchRchFrac**",3,"Float",0,1,"fraction","Fraction of this reach impacted by another reach", [NumWBN],[WBNNumRch],[WBNRchNumRch]

"**WBNRchRchIndex**",3,"Integer",0,50,,"Index of reach that impacts this reach", [NumWBN], [WBNNumRch],[WBNRchNumRch]

"**WBNRchSrcLWSFrac**",2,"Float",0,1,"fraction","fraction of waterbody network reach impacted by the source local watershed",[NumWBN],[WBNNumRch]

"**WBNRchSrcLWSIndex**",2,"Integer",0,10,"index of local watershed from source", [NumWBN],[WBNNumRch]

"**WBNRchType**",2,"String",,,,"Type of reach (Headwater, exiting, other)", [NumWBN],[WBNNumRch]

"**WBNRchWSSubFrac**",3,"Float",0,1,"fraction","Fraction of this reach impacted by watershed", [NumWBN],[WBNNumRch],[WBNRchNumWSSub]

"**WBNRchWSSubIndex**",3,"Integer",0,50,"Index of watershed that impacts this reach", [NumWBN],[WBNNumRch],[WBNRchNumWSSub]

"**WBNTemp**",1,"Float",0,35,"degrees Celsius","median temperature of stream, lake, and wetland reaches in waterbody network",[3]

"**WBNTOC**",1,"Float",0,100,"mg/L","TOC of stream, lake, and wetland reaches in waterbody network",[3]

"**WBNTSS**",1,"Float",0,1000,"mg/L","TSS of stream, lake, and wetland reaches in waterbody network",[3]

3.1.2 Variables in the SW*.SSFs

The surface water SSF files contain 25 variables that are relevant only to the surface water module.

"**ahyd_d**",0,"FLOAT",0,10,"m","hydraulic coeff, depth multiplier",

"**bhyd_d**",0,"FLOAT",0,1,"","hydraulic coeff, depth exponent",

"**ahyd_W**",0,"FLOAT",0,100,"m","hydraulic coeff, width multiplier",

"**bhyd_W**",0,"FLOAT",0,1,"","hydraulic coeff, width exponent",

"**DepthSedRes**",1,"float",10,30,"cm","underlying sediment layer depth",[NumRchType],

"**DepthBenthos**",1,"float",1,10,"cm","surficial sediment layer depth",[NumRchType],

"**d_pond**",2,"float",0,3,"m","depth of pond",[WBN],[NumRch]; a minimum of 0.5 checked in ExamsIO

"**d_wtland**",2,"float",0,2,"m","depth of wetland",[WBN],[NumRch]; a minimum of 0.05 checked in ExamsIO

"**d_epil**",2,"FLOAT",0,5,"m","depth of epilimnion",[WBN],[NumRch]; a minimum of 0.1 checked in ExamsIO

"**d_hypol**",2,"FLOAT",0,20,"m","depth of hypolimnion",[WBN],[NumRch]; a minimum of 1 checked in ExamsIO

"**E_sw**",1,"float",0,1.0e-04,"cm²/sec","sediment-water column diffusion coefficient", [NumRchType],

"**E_thermocline**",0,"FLOAT",0,0.01,"cm²/sec","thermocline diffusion coefficient",

"**rhoDSedRes**",1,"FLOAT",0.3,2.5,"g/mL","underlying sediment layer dry bulk density", [NumRchType],

"**porSedRes**",1,"FLOAT",0.1,0.9,"Lw/L","underlying sediment layer porosity",[NumRchType],

"**rhoDBenthos**",1,"FLOAT",0.03,2.2,"g/mL","surficial sediment layer dry bulk density", [NumRchType],

"**porBenthos**",1,"FLOAT",0.2,0.99,"Lw/L","surficial sediment layer porosity",[NumRchType],

"**k_PlankCMin**",0,"FLOAT",0,1.0,"yr⁻¹","Plankton carbon mineralization rate constant"; not used in this HWIR application.

"**k_SedG2**",0,"FLOAT",0,0.6,"yr⁻¹","Sediment mineralization rate constant, G2 fraction"; not used in this HWIR application.

"**k_SedG3**",0,"FLOAT",0,0.1,"yr⁻¹","Sediment mineralization rate constant, G3 fraction"; not used in this HWIR application.

"**v_bury**",1,"FLOAT",0,1000,"mm/yr","underlying sediment layer burial rate",[NumRchType]; not used in this HWIR application.

"**TrophicIndex**",1,"INTEGER",0,7,"","trophic index",[NumRchType],

"S_upstream",0,"FLOAT",0,1000,"mg/L",[upstream suspended solids concentration],

"C_upstream",1,"FLOAT",0,100,"mg/L","upstream chemical concentration",[NumChem]; not used in this HWIR application.

"Q_upstream",2,"FLOAT",0,1.0e+10,"m3/day","upstream flow","WBN",[NumRch],

3.1.3 Variables in the CPStream.SSF

The stream chemical SSF file contains 124 variables, 44 of which are relevant to the surface water module.

"ChemName",1,"String",,,,"Chemical Name",[NumChem]

"ChemActBioNumProd",1,"Integer",,,,"Number of products",[NumChem]

"ChemActBioProdCASID",2,"String",,,,"Product CASID",[NumChem],[ChemActBioNumProd]

"ChemActBioProdName",2,"String",,,,"Product Name",[NumChem],[ChemActBioNumProd]

"ChemActBioProdYield",2,"Float",,,,"moles/moles","Product Yield Coefficient", [NumChem],[ChemActBioNumProd]

"ChemActBioRate",1,"Float",,,,"1/day","Activated Biodegradation",[NumChem]

"ChemADiff",1,"Float",,,,"cm^2/s","Air Diffusion Coefficient",[NumChem]

"ChemAerBioNumProd",1,"Integer",,,,"Number of products",[NumChem]

"ChemAerBioProdCASID",2,"String",,,,"Product CASID",[NumChem],[ChemAerBioNumProd]

"ChemAerBioProdName",2,"String",,,,"Product Name",[NumChem],[ChemAerBioNumProd]

"ChemAerBioProdYield",2,"Float",,,,"moles/moles","Product Yield Coefficient",[NumChem],[ChemAerBioNumProd]

"ChemAerBioRate",1,"Float",,,,"1/day","Aerobic Biodegradation rate",[NumChem]

"ChemAnaBioNumProd",1,"Integer",,,,"Number of products",[NumChem]

"**ChemAnaBioProdCASID**",2,"String",,,,"Product CASID",[NumChem],
[ChemAnaBioNumProd]

"**ChemAnaBioProdName**",2,"String",,,,"Product Name",[NumChem],[ChemAnaBioNumProd]

"**ChemAnaBioProdYield**",2,"Float",,,,"moles/moles","Product Yield Coefficient",[NumChem],
[ChemAnaBioNumProd]

"**ChemAnaBioRate**",1,"Float",,,,"1/day","Anaerobic Biodegradation",[NumChem]

"**ChemAnaRedNumProd**",1,"Integer",,,,"Number of products",[NumChem]

"**ChemAnaRedProdCASID**",2,"String",,,,"Product CASID",[NumChem],
[ChemAnaRedNumProd]

"**ChemAnaRedProdName**",2,"String",,,,"Product Name",[NumChem],[ChemAnaRedNumProd]

"**ChemAnaRedProdYield**",2,"Float",,,,"moles/moles","Product Yield Coefficient",[NumChem],
[ChemAnaRedNumProd]

"**ChemAnaRedRate**",1,"Float",,,,"1/day","Anaerobic Reduction",[NumChem]

"**ChemDen**",1,"Float",0,,,"g/mL","Density",[NumChem]

"**Chemfoc**",0,"Float",,,,"fraction","Fraction Organic Content of Medium"

"**ChemHLC**",1,"Float",,,,"(atm m³)/mol","Henry's Law Constant",[NumChem]

"**ChemHydNumProd**",1,"Integer",,,,"Number of products",[NumChem]

"**ChemHydProdCASID**",2,"String",,,,"Product CASID",[NumChem],[ChemCatNumProd]

"**ChemHydProdName**",2,"String",,,,"Product Name",[NumChem],[ChemCatNumProd]

"**ChemHydProdYield**",2,"Float",,,,"moles/moles","Product Yield Coefficient",[NumChem],
[ChemCatNumProd]

"**ChemHydRate**",1,"Float",,,,"1/day","Catalyzed Hydrolysis",[NumChem]

"**ChemKd**",2,"Float",,,,"L/kg","Partition Coefficient for Med",[NumChem],[4]

"ChemKoc",1,"Float",,,,"mL/g","Koc",[NumChem]

"ChemKow",1,"Float",,,,"Kow",[NumChem]

"ChemMed",1,"String",,,,"Solubility Media (Soil, Sediment, Surface Water, Waste)",[4]

"ChemMolWt",1,"Float",,,,"g/mole","Molecular weight for the chemical",[NumChem]

"ChemName",1,"String",,,,"Name",[NumChem]

"ChemPh",0,"Float",,,,"pH units",[pH assumed for these properties]

"ChemSol",2,"Float",,,,"mg/L","Solubility for each media",[NumChem],[4]

"ChemTemp",0,"Float",,,,"degrees Celsius","Temperature assumed for these properties"

"ChemType",1,"string",,,,"Chemical Type (O, M, Hg, S, D)",[NumChem]

"ChemVol",1,"Float",0,,,"mL","Volume",[NumChem]

"ChemVp",1,"Float",,,,"torr","Vapor Pressure",[NumChem]

"ChemWDiff",1,"Float",,,,"cm²/s","Water Diffusion Coefficient",[NumChem]

"NumChem",0,"Integer",,,,"Number of chemicals described"

3.2 Global Results Files

Each module generates one global results file (GRF) per simulation. Four module grf's are used for input to the surface water module -- the atmospheric results file ar*.grf, the source results file sr.grf, the watershed results file ws.grf, and the groundwater results file aq.grf. In addition, the surface water module produces a results file for each water body at a site (sw*.grf, where * stands for the water body number at a site). These are ASCII, comma-delimited files that are accessed by the modules using a specially-provided dynamic link library. Each file has a corresponding data dictionary file in the /GRF/ subdirectory (i.e., ar.dic, sr.dic, ws.dic, aq.dic, and sw.dic). The dictionary files list the variable names along with their dimensions, data type (i.e., character or "string", real or "float," or integer), minimum and maximum values, units, and a brief description. For some arrays, the maximum number of entries are also given.

3.2.1 Variables in the AR*.SSF

The atmospheric results file contains 18 variables, 9 of which are used by the surface water module.

VapWDep,2,FLOAT,0,100000,g/m2/d, vapor wet deposition flux, [NumAir][VapWDepNY]

VapWDepYR,2,Integer,0,100000,Year, year corresponding to vapor wet deposition flux value, [NumAir] [VapWDepNY]

VapWDepNY,1,Integer,0,100000,, number of annual vapor wet deposition flux values, [NumAir]

ParDDep,2,FLOAT,0,100000,g/m2/d, particle dry deposition flux, [NumAir][ParDDepNY]

ParDDepYR,2,Integer,0,100000,Year, year corresponding to particle dry deposition flux value, [NumAir][ParDDepNY]

ParDDepNY,1,Integer,0,100000,, number of particle dry deposition flux values, [NumAir]

ParWDep,2,FLOAT,0,100000,g/m2/d, particle wet deposition flux, [NumAir][ParWDepNY]

ParWDepYR,2,Integer,0,100000,Year,year corresponding to particle dry deposition flux value, [NumAir] [ParWDepNY]

ParWDepNY,1,Integer,0,100000,, number of particle dry deposition flux values, [NumAir]

3.2.2 Variables in the SR.SSF

The waste management unit (source) results file contains 39 variables, 7 of which are used by the surface water module.

"Runoff",2,"float",0,1e04,"m3/d","runoff",[NumLWS],[NyrMet]

"SWLoadChem",2,"float",0,1e08,"g/d","chemical load to waterbody",[NumLWS],[SWLoadChemNY]

"SWLoadChemYR",2,"integer",1,10000,"year","year associated with output",[NumLWS],[SWLoadChemNY]

"SWLoadChemNY",1,"integer",1,10000,"","number of years in outputs",[NumLWS]

"SrcOvl",0,"logical"," flag for overland flow presence"

"SrcH2O",0,"logical","flag for surface water presence"

"NyrMet",0,"integer",1,100,"year","number of years in the available met record"

3.2.3 Variables in the WS.SSF

The watershed results file contains 15 variables, 7 of which are used by the surface water module.

"NyrMet",0,"integer",1,100,"year","number of years in the available met record"

"RunoffR",2,"float",0,10000,"m3/d","runoff flow to waterbody",[NumWSSub],[NyrMet]

"BFann",1,"float",0,10000,"m3/d","long-term avg baseflow to waterbody",[NumWSSub]

"SWLoadChemR",2,"float",0,100000000,"g/d","chemical load (deposition only) to waterbody",[NumWSSub],[SWLoadChemRNY]

"SWLoadChemRYR",2,"integer",1,10000,"year","year associated with output",[NumWSSub],[SWLoadChemRNY]

"SWLoadChemRNY",1,"integer",1,10000,"","number of years in outputs",[NumWSSub]

"SWLoadSolidR",2,"float",0,10000000000,"g/d","total suspended solids (runoff)",[NumWSSub],[NyrMet]

3.2.4 Variables in the AQ.SSF

The groundwater (aquifer) results file contains 9 variables, 4 of which are used by the surface water module.

"AquRchMassFlux",2,Float,0,1000000, g/yr, Mass Flux from Aquifer to Reach, [NumChem],[AquRchMassFluxNY]

"AquRchMassFluxNY",1,Integer,0,10000, , Number of Time - Mass-Flux-to-Reach Pairs, [NumChem]

AquRchMassFluxYR,2,Integer,0,10000, year, Time of Mass Flux from Aquifer to Reach, [NumChem], [AquRchMassFluxNY]

AquRchWaterFlux,0,Float,0,1e8,m3/day, Total GW Flux to Reach

3.2.5 Variables in the SW*.SSF

The surface water results file contains 20 variables that are used by the exposure modules.

WBNConcBenthDiss,3,Float,0,1000000,mg/L, Dissolved chemical concentration in the surficial benthic layer, [WBNNumChem],[WBNNumRch],[WBNConcBenthDissNY]

WBNConcBenthDissNY,2,Integer,0,10000,, Number of dissolved chemical concentration values in the surficial benthic layer, [WBNNumChem],[WBNNumRch]

WBNConcBenthDissYr,3,Integer,0,10000,year, Year corresponding to dissolved chemical concentration in benthic layer, [WBNNumChem],[WBNNumRch],[WBNConcBenthDissNY]

WBNConcBenthTot,3,Float,0,1000000,ug/g, Total chemical concentration in the surficial benthic layer, [WBNNumChem],[WBNNumRch],[WBNConcBenthTotNY]

WBNConcBenthTotNY,2,Integer,0,10000,, Number of total chemical concentration values in the surficial benthic layer, [WBNNumChem],[WBNNumRch]

WBNConcBenthTotYr,3,Integer,0,10000,year,Year corresponding to total chemical concentration in benthic layer, [WBNNumChem],[WBNNumRch],[WBNConcBenthTotNY]

WBNConcWaterDiss,3,Float,0,1000000,mg/L, Dissolved chemical concentration in the water column, [WBNNumChem],[WBNNumRch],[WBNConcWaterDissNY]

WBNConcWaterDissNY,2,Integer,0,10000,, Number of dissolved chemical concentration values in the water column, [WBNNumChem],[WBNNumRch]

WBNConcWaterDissYr,3,Integer,0,10000,year, Year corresponding to dissolved chemical concentration in the water column, [WBNNumChem],[WBNNumRch],[WBNConcBenthDissNY]

WBNConcWaterTot,3,Float,0,1000000,mg/L, Total chemical concentration in the water column, [WBNNumChem],[WBNNumRch],[WBNConcWaterTotNY]

WBNConcWaterTotNY,2,Integer,0,10000,, Number of total chemical concentration values in the water column, [WBNNumChem],[WBNNumRch]

WBNConcWaterTotYr,3,Integer,0,10000,year, Year corresponding to dissolved chemical concentration in the water column, [WBNNumChem],[WBNNumRch],[WBNConcBenthTotNY]

WBnfocBenth,2,Float,0,0.5,fraction, Organic carbon content of benthic sediments, [WBNNumRch,WBnfocBenthNY]

WBnfocBenthNY,1,Integer,0,10000,, Number of organic carbon content values, [WBNNumRch]

WBnfocBenthYr,2,Integer,0,10000,year, Year corresponding to organic content values, [WBNNumRch,WBnfocBenthNY]

WBNNumChem,0,Integer,1,10,, Number of chemicals in output file,

WBNTSSWater,2,Float,0,70000,mg/L, Total suspended solids concentration in the water column, [WBNNumRch,WBNTSSWaterNY]

WBNTSSWaterNY,1,Integer,0,10000,, Number of suspended solids concentration values, [WBNNumRch]

WBNTSSWaterYr,2,Integer,0,10000,year, Year corresponding to suspended solids values, [WBNNumRch,WBNTSSWaterNY]

3.3 Surface Water Module EXAMS Files

With each execution of a water body network, ExamsIO produces three batch files for use by EXAMS – the run file “hwirexp.exe,” the chemical file “hwirexp1.chm,” and the environment file “hwirexp.env.” If two or more chemicals are included in the simulation, then separate files are created for each chemical (hwirexp2.chm, hwirexp3.chm, etc.). EXAMS subsequently produces a batch results file “hwirexp.xms” for use by the ExamsIO postprocessor. These are all formatted ASCII files, accessed using standard Fortran 90/95 read statements.

3.3.1 Variables in hwirexp1.chm

One EXAMS chemical file is written for each chemical simulated. The file structure and variables are the same for each chemical. The chemical file is composed of 25 records, each containing one or more variables. The first set of records is read once and the variables represent properties of the overall chemical. The second set of records is read once for each ionic species

simulated, and the variables represent properties of that species only. For the HWIR implementation, the species flags for all ionic species are set to 0, and the total chemical is simulated as a neutral species. Chemical values are weighted to account for any ionic species properties at the given water body temperature and pH. Short definitions and units are given; more complete information is available in the EXAMS II data dictionary in Burns (1997).

Record 1 [Format (1(A50))]

CHEMNA(iChem), Chemical name.

Record 2 [Format (7(I1,1X))]

(**SPFLG**(iIon,iChem),iIon = 1,7), Ionic species flags. Neutral chemical species is represented by iIon = 1. All others are set to 0 in the HWIR application.

Record 3 [Format (8(E10.3))]

MWT(iChem), Molecular weight, g/mole.

KOC(iChem), Organic carbon partition coefficient, (mg/kg-organic carbon)/(mg/L-water).

KOW(iChem) Octanol-water partition coefficient, (mg/L-octanol)/(mg/L-water).

Record 4 [Format (8(E10.3))]

MP(iChem), Melting point, EC.

HENRY(iChem), Henry's Law constant, atmosphere-m³/mole.

EHEN(iChem), Enthalpy term for Henry's Law constant (set to 0), kcal/mole.

VAPR(iChem), Vapor pressure, torr.

EVPR(iChem) Molar heat of vaporization (set to 0), kcal/mole.

The rest of the chemical records are repeated as a block for each ionic species "iIon" simulated.

Record 5 [Format (8(E10.3))]

SOL(iIon,iChem), Solubility, mg/L.

ESOL(iIon,iChem), Enthalpy term for solubility, kcal/mole

KPS(iIon,iChem), Partition coefficient for sediment solids (set to 0), (mg/kg-solids)/(mg/L-pore water).

KPB(iIon,iChem), partition coefficient for biomass (specify 0, calculated internally), (mg/kg-biomass)/(mg/L-water).

KPDOC(iIon,iChem), partition coefficient for DOC (specified as 0, calculated internally), (mg/kg-DOC)/(mg/L-water).

Record 6 [Format (8(E10.3))]

This record is read by EXAMS only for ionic species; it is skipped in this HWIR application.

PK(iIon - 1,iChem), Negative of base-10 logarithm of acid/base dissociation constants.

EPK(iIon - 1,iChem), Enthalpy term for pK, kcal/mole.

KIEC(iIon - 1,iChem) Coefficient relating ion exchange capacity to partitioning, Kp/(meq/100 g dry), where Kp units are (mg/kg-solids)/(mg/L-water).

Record 7 [Format (8(E10.3))]

(**QUANT**(iForm,iIon,iChem),iForm = 1,3) Reaction quantum yield for direct photolysis, dimensionless. Not used in HWIR application.

Record 8 [Format (8(E10.3))]

(**ABSOR**(iWave,iIon,iChem),iWave = 1,46) Mean decadic molar light extinction coefficients in 46 wavelength intervals, $\text{cm}^{-1} (\text{mole/L})^{-1}$. Not used in HWIR application.

Record 9 [Format (8(E10.3))]

KDP(iIon,iChem), Annual-average direct photolysis rate constant under cloudless conditions at reference latitude, hr^{-1} . Not used in HWIR application.

RFLAT(iIon,iChem), Reference latitude at which the photolysis rate constant KDPG was measured, degrees. Not used in HWIR application.

LAMAX(iIon,iChem) Wavelength of maximum absorption of light, nanometers. Not used in HWIR application.

Record 10 [Format (8(E10.3))]

(KAH(iForm,iIon,iChem),iForm = 1,3) Second-order rate constant for acid-catalyzed hydrolysis, per mole [H⁺] per hour. Not used in HWIR application.

Record 11 [Format (8(E10.3))]

(EAH(iForm,iIon,iChem),iForm = 1,3) Arrhenius activation energy for acid-catalyzed hydrolysis of chemical, kcal/mole. Not used in HWIR application.

Record 12 [Format (8(E10.3))]

(KNH(iForm,iIon,iChem),iForm = 1,3) First-order rate constant for neutral hydrolysis of chemical, hr⁻¹.

Record 13 [Format (8(E10.3))]

(ENH(iForm,iIon,iChem),iForm = 1,3) Arrhenius activation energy for neutral hydrolysis of chemical, kcal/mole. Not used in HWIR application.

Record 14 [Format (8(E10.3))]

(KBH(iForm,iIon,iChem),iForm = 1,3) Second-order rate constant for base-catalyzed hydrolysis, per mole [OH⁻] per hour. Not used in HWIR application.

Record 15 [Format (8(E10.3))]

(EBH(iForm,iIon,iChem),iForm = 1,3) Arrhenius activation energy for base-catalyzed hydrolysis of chemical, kcal/mole. Not used in HWIR application.

Record 16 [Format (8(E10.3))]

(KOX(iForm,iIon,iChem),iForm = 1,3) Second-order rate constant for free-radical oxidation of chemical, per mole [OXRAD] per hour. Not used in HWIR application.

Record 17 [Format (8(E10.3))]

(**EOX**(iForm,iIon,iChem),iForm = 1,3) Arrhenius activation energy for oxidation of chemical, kcal/mole. Not used in HWIR application.

Record 18 [Format (8(E10.3))]

(**K1O2**(iForm,iIon,iChem),iForm = 1,3) Second-order rate constant for singlet oxygen photo-oxygenation of chemical, per mole [$^1\text{O}_2$] per hour. Not used in HWIR application.

Record 19 [Format (8(E10.3))]

(**EK1O2**(iForm,iIon,iChem),iForm = 1,3) Arrhenius activation energy for singlet oxygen photo-oxygenation of chemical, kcal/mole. Not used in HWIR application.

Record 20 [Format (8(E10.3))]

(**KRED**(iForm,iIon,iChem),iForm = 1,3) Second-order rate constant for reduction of chemical, per mole [REDAG] per hour.

Record 21 [Format (8(E10.3))]

(**ERED**(iForm,iIon,iChem),iForm = 1,3) Arrhenius activation energy for reduction of chemical, kcal/mole. Not used in HWIR application.

Record 22 [Format (8(E10.3))]

(**KBACW**(iForm,iIon,iChem),iForm = 1,4) Second-order rate constant for water column bacterial degradation of chemical, $(\text{cell/mL})^{-1} \text{ hr}^{-1}$.

Record 23 [Format (8(E10.3))]

(**QTBAW**(iForm,iIon,iChem),iForm = 1,4) Q_{10} values used to adjust bacterioplankton biodegradation rates for temperature, dimensionless. Not used in HWIR application.

Record 24 [Format (8(E10.3))]

(**KBACS**(iForm,iIon,iChem),iForm = 1,4) Second-order rate constant for benthic sediment bacterial degradation of chemical, $(\text{cell/mL})^{-1} \text{ hr}^{-1}$.

Record 25 [Format (8(E10.3))]

(**QTBAS**(iForm,iIon,iChem),iForm = 1,4) Q_{10} values used to adjust benthic biodegradation rates for temperature, dimensionless. Not used in HWIR application.

3.3.2 Variables in hwirexp.env

The EXAMS environment file is composed of 54 records, each containing one or more variables. The first set of records is read once, and the values are constant. The second set of records is read 13 times, once for each month and once for annual-average values. Short definitions and units are given; more complete information is available in the EXAMS II data dictionary in Burns (1997).

Record 1 [Format(1(A50), I10)]

ECONAM, Name of aquatic water body.

WBNId Water body identification number.

Record 2 [Format(16(I5))]

KOUNT, Number of compartments used to define water body.

Record 3 [(80A1)]

(**TYPE**(iSeg),iSeg = 1,KOUNT), Compartment type, letter code. Littoral, Epilimnion, Hypolimnion, Benthic.

Record 4 [(8(F10.2))]

LAT, Geographic latitude of water body, degrees and tenths.

LONG, Geographic longitude of water body, degrees and tenths.

ELEV, Ground station elevation, meters above mean sea level.

Record 5 [(8(E10.3))]

(**VOL**(iSeg),iSeg = 1,KOUNT), Volume of water body compartments, m^3 . Zero values are entered, and the volumes are calculated internally.

Record 6 [(8(E10.3))]

(**AREA**(iSeg),iSeg = 1,KOUNT), Surface area of water body compartment, m². Zero values are entered for stream reaches, and the areas are calculated internally. Actual surface areas are entered for pond, wetland, lake, and bay reaches.

Record 7 [(8(E10.3))]

(**DEPTH**(iSeg),iSeg = 1,KOUNT), Average vertical depth of water body compartment, m. Zero values are entered for stream water body compartments, and the values are calculated internally.

Record 8 [(8(F10.2))]

(**XSA**(iSeg),iSeg = 1,KOUNT), Cross-sectional area of a compartment along flow path, m². Zero values are entered and the areas are calculated internally from depths and widths.

Record 9 [(8(F10.2))]

(**LENG**(iSeg),iSeg = 1,KOUNT), Length of a compartment, m. Used to compute volume and surface area of stream compartments. Zero values are entered for ponds, wetlands, lakes, and bays; volume for these compartments are calculated from surface area and depth.

Record 10 [(8(F10.2))]

(**WIDTH**(iSeg),iSeg = 1,KOUNT), Width of a compartment, m. Zero values are entered for all compartments, and values are calculated internally for stream compartments. Used to compute volume and surface area of stream compartments.

Record 12 [Format(16(I5))]

NSPEC1, Number of advective flow paths between compartments. This is calculated by ExamsIO from HWIR specifications.

Record 13 [Format(16(I5))]

(**JFRAD**(iPath),iPath = 1,NSPEC1), Compartment from which advection is taken for flow pathway "iPath."

Record 14 [Format(16(I5))]

(**ITOAD**(iPath),iPath = 1,NSPEC1), Compartment to which advection is directed for flow pathway "iPath."

Record 15 [(8(F10.2))]

(**ADVPR**(iPath),iPath = 1,NSPEC1), Proportion of flow advected from compartment JFRADG that enters ITOADG for flow pathway “iPath.”

Record 16 [Format(16(I5))]

NSPEC2, Number of dispersive transport paths between compartments. This is calculated by ExamsIO from HWIR specifications.

Record 17 [Format(16(I5))]

(**JTURB**(iPath),iPath = 1,NSPEC2), First compartment exchanging dispersive flows for dispersive pathway “iPath.”

Record 18 [Format(16(I5))]

(**ITURB**(iPath),iPath = 1,NSPEC2), Second compartment exchanging dispersive flows for dispersive pathway “iPath.”

Record 19 [(8(E10.3))]

(**XSTUR**(iPath),iPath = 1,NSPEC2), Cross-sectional area of exchange interface for dispersive pathway “iPath.”, m².

Record 20 [(8(E10.3))]

(**CHARL**(iPath),iPath = 1,NSPEC2), Characteristic mixing length normal to the exchange interface linking compartments, m.

The following records (21 - 54) are repeated as a block 13 times, once for each month, and then for annual average conditions.

Record 21 [(8(E10.3))]

(**DSP**(iPath,iMonth),iPath = 1,NSPEC2), Dispersion coefficient for exchange path “iPath,” month “iMonth,” m²/hr.

Record 22 [(8(E10.2))]

(**WIND**(iSeg,iMonth),iSeg = 1,KOUNT), Average wind velocity at a reference height of 10 cm above the water surface of compartment, m/sec.

Record 23 [(8(E10.3))]

(**STFLO**(iSeg,iMonth),iSeg = 1,KOUNT), Upstream inflow entering water body compartment, m³/hr.

Record 24 [(8(E10.3))]

(**STSED**(iSeg,iMonth),iSeg = 1,KOUNT), Stream-borne sediment load entering water body compartment, kg/hr.

Record 25 [(8(E10.3))]

(**NPSFL**(iSeg,iMonth),iSeg = 1,KOUNT), Nonpoint source water flow entering water body compartment, m³/hr.

Record 26 [(8(E10.3))]

(**NPSED**(iSeg,iMonth),iSeg = 1,KOUNT), Nonpoint source sediment loads entering water body compartment, kg/hr.

Record 27 [(8(E10.3))]

(**SEEPS**(iSeg,iMonth),iSeg = 1,KOUNT), Subsurface water flow entering water body benthic compartment, m³/hr.

Record 28 [(8(E10.2))]

(**RAIN**(iMonth)), Average monthly rainfall, mm/month.

Record 29 [(8(E10.2))]

(**CLOUD**(iMonth)) Average monthly cloud cover, tenths of full sky cover, dimensionless. Not used in HWIR application.

Record 30 [(8(E10.2))]

(**OZONE**(iMonth)), Average monthly ozone content of atmosphere, cm NTP. Not used in HWIR application.

Record 31 [(8(E10.2))]

(**RHUM**(iMonth)), Average monthly relative humidity during daylight hours, percent. Not used in HWIR application.

Record 32 [(8(E10.2))]

(**ATURB**(iMonth)), Average monthly equivalent aerosol layer thickness, km. Not used in HWIR application.

Record 33 [(80(A1))]

(**AIRTY**(iMonth)) Average monthly air mass type (Rural, Urban, Maritime, or Tropospheric). Not used in HWIR application.

Record 34 [(8(E10.2))]

(**DFAC**(iSeg,iMonth),iSeg = 1,KOUNT), Ratio of optical path to vertical depth in compartment, defaulting to 1.19, dimensionless. Not used in HWIR application.

Record 35 [(8(E10.2))]

(**EVAP**(iSeg,iMonth),iSeg = 1,KOUNT), Monthly evaporative loss rate, mm/month.

Record 36 [(8(E10.2))]

(**SUSED**(iSeg,iMonth),iSeg = 1,KOUNT), Average monthly suspended solids concentration in the water column compartments, mg/L. This value is overridden in this HWIR application by internal calculations of solids based on watershed erosion loadings.

Record 37 [(8(E10.2))]

(**BULKD**(iSeg,iMonth),iSeg = 1,KOUNT) Average monthly benthic bulk density, or fresh weight per unit volume of sediments, g/mL. It is calculated in ExamsIO from porosity and dry bulk density.

Record 38 [(8(E10.2))]

(**PCTWA**(iSeg,iMonth),iSeg = 1,KOUNT), “Percent water” in sediments of benthic compartments. This conventional soil science term is actually the ratio of fresh weight to dry weight times 100. It is calculated in ExamsIO from porosity and dry bulk density.

Record 39 [(8(E10.3))]

(**FROC**(iSeg,iMonth),iSeg = 1,KOUNT), Average monthly organic carbon content of solids in compartment as a fraction of dry weight.

Record 40 [(8(E10.2))]

(**CEC**(iSeg,iMonth),iSeg = 1,KOUNT), Average monthly cation exchange capacity of solids in compartment, meq/100 g (dry). Not used in HWIR application.

Record 41 [(8(E10.2))]

(**AEC**(iSeg,iMonth),iSeg = 1,KOUNT), Average monthly anion exchange capacity of solids in compartment, meq/100 g (dry). Not used in HWIR application.

Record 42 [(8(E10.2))]

(**TCEL**(iSeg,iMonth),iSeg = 1,KOUNT), Average monthly water temperature of compartment, degrees C.

Record 43 [(8(E10.2))]

(**PH**(iSeg,iMonth),iSeg = 1,KOUNT), Average monthly pH of compartment, used to derive the hydronium ion [H₃O⁺] concentration.

Record 44 [(8(E10.2))]

(**POH**(iSeg,iMonth),iSeg = 1,KOUNT), Average monthly pOH of compartment, used to derive the hydroxide ion [OH⁻] concentration.

Record 45 [(8(E10.3))]

(**OXRAD**(iMonth)), Average monthly concentration of chemical oxidants in near-surface waters, used by EXAMS to calculate values in compartments, moles/L. Not used in HWIR application.

Record 46 [(8(E10.3))]

(**BACPL**(iSeg,iMonth),iSeg = 1,KOUNT), Average monthly concentration of bacterioplankton capable of degrading the chemical of interest, count/mL. Set to 1.0 in HWIR application so that the second order rate constant KBACW becomes a pseudo-first order rate constant.

Record 47 [(8(E10.3))]

(**BNBAC**(iSeg,iMonth),iSeg = 1,KOUNT), Average monthly concentration of benthic bacteria capable of degrading the chemical of interest, count/100g dry sediment. Set to (PCTWA-100) in HWIR application so that the second order rate constant KBACS becomes a pseudo-first order rate constant.

Record 48 [(8(E10.2))]

(**PLMAS**(iSeg,iMonth),iSeg = 1,KOUNT), Average monthly plankton concentration in compartment, mg (dry weight)/L.

Record 49 [(8(E10.2))]

(**BNMAS**(iSeg,iMonth),iSeg = 1,KOUNT), Average monthly biomass of small benthos in compartment, g(dry)/m². Not used in HWIR application.

Record 50 [(8(E10.3))]

(**KO2**(iSeg,iMonth),iSeg = 1,KOUNT), Average monthly oxygen exchange constant at 20 EC, calculated for surface water compartments from wind speed, current velocity, and depth by ExamsIO., cm/hour.

Record 51 [(8(E10.2))]

(**DOC**(iSeg,iMonth),iSeg = 1,KOUNT), Average monthly dissolved organic carbon concentration in compartment, mg/L. Used in HWIR application for complexing chemical, but not for light absorption.

Record 52 [(8(E10.2))]

(**CHL**(iSeg,iMonth),iSeg = 1,KOUNT), Average monthly chlorophyll concentration in compartment, mg/L. Not used in HWIR application.

Record 53 [(8(E10.2))]

(**DISO2**(iSeg,iMonth),iSeg = 1,KOUNT), Average monthly dissolved oxygen concentration in compartment, mg/L. Not used in HWIR application.

Record 54 [(8(E10.3))]

(REDAG(iSeg,iMonth),iSeg = 1,KOUNT), Average monthly concentration of reducing agents in compartment, moles/L. Set to 1.0 in HWIR application so that the second order rate constant KRED becomes a pseudo-first order rate constant.

3.3.3 Commands and Variables in hwirexp.exe

The EXAMS batch run file sets up and controls the EXAMS implementation. Each EXAMS implementation is composed of an initialization phase and simulation phase 1. Some implementations also include a simulation phase 2. Simulation phase 1 covers the period when the source and all environmental media (air, watershed, and ground water) can provide loadings to the surface water. Phase 2 covers the period when only the ground water is providing loadings to the surface water.

The EXAMS batch run file is composed of an indeterminate number of records, each containing a single command that sets a variable to a particular value. The first set of records initializes the simulation; the commands are issued once at the beginning of the simulation, and variable values remain constant within Exams until they are updated by later commands. The second set of records is read once for each simulated year in Phase 1 of the simulation. The third set of records is reinitializes some environmental variables for Phase 2 of the simulation. The fourth set of records is issued periodically throughout Phase 2, as controlled by data from the ground water simulation.

Initialization of the simulation – Command blocks 1 through 9 initialize the Exams application.

Command Block 1:

The first command is issued by subroutine InitChem:

"set kchem to ", **NumChem**

NumChem is the number of chemicals simulated, and is found in cpStream.ssf. The value is 1 for all present HWIR applications except mercury. Mercury simulations are composed of three interacting components – divalent mercury, methyl mercury, and elemental mercury.

Command Block 2 (optional):

If any reaction products are to be simulated, then the following commands are issued by subroutine InitChem for each transformation pathway. In the present HWIR application, transformation pathways are used only for simulating mercury. For all other chemicals, these commands are bypassed.

```
"set rform(", ipath, ") to ", RFORM(iPath)
"set chpar(", ipath, ") to ", CHPAR(iPath)
"set nproc(", ipath, ") to ", NPROC(iPath)
"set tprod(", ipath, ") to ", TPROD(iPath)
"set yield(", ipath, ") to ", YIELD(iPath)
"set eayld(", ipath, ") to ", EAYLD(iPath)
```

The variable "ipath" is the transformation pathway number, which is accumulated as a counter in ExamsIO. RFORM is the molecular form or ionic species number of the reaction product for transformation "ipath." In this HWIR application, RFORM is always set to 1, denoting the neutral species. CHPAR is the chemical number for the parent (source) chemical in reaction "ipath." TPROD is the chemical number for the daughter (product) chemical in reaction "ipath." NPROC is the type of process transforming CHPAR into TPROD. Those available to this HWIR application are 2 (neutral hydrolysis), 7 (water column biodegradation), 8 (benthic biodegradation), and 9 (chemical reduction). YIELD is the molar product yield from reaction "ipath," in moles TPROD produced per mole CHPAR consumed. EAYLD is the activation energy to compute the transformation product yield for reaction "ipath." In this HWIR application, EAYLD is set to 0, giving no temperature dependence.

Command Block 3:

This block of commands is issued from subroutine PreProc.

```
"set mode to ", MODE
"set tcode to ", TCODE
"set tinit to ", TINIT
"set tend to ", TEND
"set cint to ", CINT
"set reler to ", RELER
"set abser to ", ABSER
```

MODE sets the operating mode of the EXAMS simulation. In this HWIR application, MODE is set to 2, which simulates set periods of time using invariant (annual-average) loading and environmental conditions. While pulse loads are allowed in MODE 2, none are specified in this HWIR application. A succession of yearly periods (simulation segments) are set up, each with its constant set of loadings and environmental conditions. TCODE is the simulation time code, here set to 3 indicating units of months. TINIT and TEND are the initial and ending time for a simulation segment. These are set to 0 and 12 months, respectively, bracketing the first simulation segment. CINT is the print interval, set to 4 months giving output times of 0, 4, 8, and 12 months for each simulated year. ABSER and RELER are the absolute and relative error tolerance for the EXAMS integrators. For the HWIR application, they are set to 10^{-15} and 10^{-13} , respectively.

Command Block 4

This block of commands is issued from subroutine PreProc. The first two commands are repeated together for each chemical simulated, in which the index "iChem" varies from 1 to NumChem. In this HWIR application, only mercury simulations involve multiple chemicals. The third command is read once.

```
"set mchem to ", iChem  
"read chemical ", CHMFileName(iChem)
```

```
"read environment ", ENVFileName
```

The index iChem is the working chemical number assigned for an Exams simulation. CHMFileName is the name of the batch chemical file that Exams will read for information about chemical "iChem." The file name is "hwirexp*.chm," where * is the index "iChem." For all chemicals except mercury, the file "hwirexp1.chm" is the only chemical file created and read. ENVFileName is the name of the batch environment file that Exams reads for information about the water body to be simulated. The file name is "hwirexp.env."

Command Block 5

This command is issued from subroutine PreProc. The command is issued only if the fractional change in its previous RAIN setting is greater than ToleranceQ, which is set in ExamsIO to 0.001. Changes of less than 0.1%, then, are considered insignificant and Exams will continue its simulation using the previous value of RAIN. The index "3" is the ExamsIO array storage location for the present year's rainfall value.

```
"set RAIN(13) to", RAIN(3)
```

RAIN(13) is the yearly-average rainfall amount applied to the entire water body network, in mm/month.

Command Block 6

This block of commands is issued from subroutines InFlow and InAqLoad; it is repeated for each reach in the water body network. For a particular reach, the index "iSWSeg" gives the Exams surface water compartment number and "iSResSeg" gives the Exams lower benthic compartment number. The index "3" is the ExamsIO array storage location for the present year's flow or loading value. Loading variables are also indexed by "iChem." Individual loading commands are repeated for each separate chemical included in the HWIR simulation. In this HWIR application, the number of chemicals is always set to 1 (while this module treats mercury as three

chemical components, loadings are generated by the other HWIR modules only for divalent mercury).

Each command is issued only if the fractional change in the variable from its previous setting is greater than *ToleranceQ*.

```
"set NPSFL(" ,iSWSeg," ,*) to " , NPSFL(iSWSeg,3)
"set NPSED(" ,iSWSeg," ,*) to " , NPSED(iSWSeg,3)
"set NPSLD(" ,iSWSeg," ,iChem," ,*) to " , NPSLD(iSWSeg,iChem,3)
"set DRFLD(" ,iSWSeg," ,iChem," ,*) to " , DRFLD(iSWSeg,iChem,3)
"set EVAP(" ,iSWSeg," ,*) to " , EVAP(iSWSeg,3)
"set PCPLD(" ,iSWSeg," ,iChem," ,*) to " , PCPLD(iSWSeg,iChem,3)
"set SEELD(" ,iResSeg," ,iChem," ,*) to " , SEELD(iResSeg,iChem,3)
```

NPSFL is the nonpoint source runoff flow into compartment "iSWSeg," in m³/hour. NPSED is the nonpoint source sediment load in runoff to compartment "iSWSeg," in kg/hour. NPSLD is the nonpoint source chemical loading in runoff to compartment "iSWSeg," in kg/hour. DRFLD is the Exams variable for drift loading to compartment "iSWSeg," in kg/hour; it is used here to convey direct source runoff loading rather than drift loading. EVAP is the evaporative water loss from compartment "iSWSeg," in mm/month. PCPLD is the chemical loading in rainfall to compartment "iSWSeg," in kg/hour. Here, this loading includes vapor wet deposition, particulate wet deposition, and particulate dry deposition. SEELD is the groundwater seepage loading to compartment "iResSeg," in kg/hour.

Command Block 7

This block of commands is issued from subroutine *StreamQ*, and is repeated for each stream reach in the water body network. The index "iSWSeg" gives the Exams surface water compartment number corresponding to the reach. The index "3" is the ExamsIO array storage location for the present year's hydrogeometric value.

The first four commands are issued only if the fractional change in the volume from its previous setting is greater than *ToleranceQ*, which is set in ExamsIO to 0.001. The last command is issued only if the fractional change in its previous KO2 setting is greater than *ToleranceQ*.

```
"set AREA(" , iSWSeg," ) to " , AREA(iSWSeg)
"set DEPTH(" , iSWSeg," ) to " , DEPTH(iSWSeg)
"set WIDTH(" , iSWSeg," ) to " , WIDTH(iSWSeg)
"set VOL(" , iSWSeg," ) to " , VOL(iSWSeg)
"set KO2(" , iSWSeg," ,13) to " , KO2(iSWSeg,3)
```


AREA is the surface area of water body compartment "iSWSeg," in m². DEPTH is the average vertical depth of compartment "iSWSeg," in m, WIDTH is the width of compartment "iSWSeg," in m, VOL is the volume of compartment "iSWSeg," in m³, and KO2 is the oxygen exchange constant (reaeration) into compartment "iSWSeg," in cm/hour.

Command Block 8

This block of commands is issued from subroutine PreProc; it is repeated for each reach in the water body network. For a particular reach, the index "iSWSeg" gives the Exams surface water compartment number. The second command is issued only for a lake reach; "iSWSeg+1" gives the Exams hypolimnion compartment number.

```
"set SUSEDG(", iSWSeg,",13) to ", TSSRch(iRch,iHydroYear)
"set SUSEDG(", iSWSeg+1,",13) to ", TSSRch(iRch,iHydroYear)
```

SUSED is the total suspended solids concentration in surface water compartments, in mg/L.

Command Block 9

This command is issued a single time from subroutine PreProc:

```
"run"
```

The run command marks the completion of the initialization phase and the beginning of the Exams simulation.

Control of simulation phase 1 – For each Phase 1 simulation year, command blocks 5, 6, 7, and 8 are repeated in order, along with command block 10. The simulation years are incremented using counter "iYear" from SimSWInit1 to SimSWEnd1.

Command Block 10

This command block is issued at the end of each Phase 1 simulation year.

```
"continue"
TEND
```

The variable "TEND" is calculated as 12 times the counter "iYear." and marks the end of the present simulation segment, in total months of elapsed simulation time.

Initialization of simulation phase 2 – Command blocks 11 through 15 initialize Phase 2 of the Exams simulation.. Hydrologic variables are set to the long-term average values. These values were calculated earlier and stored in position 1 of the arrays.

Command Block 11

```
"set CINT to ", CINT
```

CINT is the print interval, reset here to 12 months giving output times of 0 and 12 months for each simulated year.

Command Block 12

```
"set RAIN(13) to", RAIN(1)
```

This sets the long-term average rainfall for the entire water body network, in cm/hour.

Command Block 13

This block of commands is issued from subroutine PreProc, and is repeated for each reach in the water body network. For a particular reach, the index "iSWSeg" gives the Exams surface water compartment number and "iSResSeg" gives the Exams lower benthic compartment number. The index "1" is the ExamsIO array storage location for the long-term average hydrological value. Loading variables are also indexed by "iChem." Individual loading commands are repeated for each separate chemical included in the HWIR simulation.

```
"set WIND(", iSWSeg, ",*) to ", WIND(iSWSeg,1)
```

```
"set TCEL(", iSWSeg, ",*) to ", TCEL(iSWSeg,1)
```

```
"set EVAP(", iSWSeg, ",*) to ", EVAP(iSWSeg,1)
```

```
"set NPSFL(", iSWSeg, ",*) to ", NPSFL(iSWSeg,1)
```

```
"set NPSED(", iSWSeg, ",*) to ", NPSED(iSWSeg,1)
```

For each chemical "iChem":

```
"set NPSLD(", iSWSeg, ",", iChem, ",*) to 0.0"
```

```
"set DRFLD(", iSWSeg, ",", iChem, ",*) to 0.0"
```

```
"set PCPLD(", iSWSeg, ",", iChem, ",*) to 0.0"
```

WIND is the annual-average wind speed 10 cm above compartment "iSWSeg," in m/sec. TCEL is the temperature of compartment "iSWSeg," in degrees Celcius. EVAP is the evaporative water loss from compartment "iSWSeg," in mm/month. NPSFL is the nonpoint source runoff flow into compartment "iSWSeg," in m³/hour. NPSED is the nonpoint source sediment load in runoff to

compartment "iSWSeg," in kg/hour. NPSLD is the nonpoint source chemical loading in runoff to compartment "iSWSeg," in kg/hour. DRFLD is the Exams variable for drift loading to compartment "iSWSeg," in kg/hour; it is used here to convey direct source runoff loading rather than drift loading. PCPLD is the chemical loading in rainfall to compartment "iSWSeg," in kg/hour. Here, this loading includes vapor wet deposition, particulate wet deposition, and particulate dry deposition.

Command Block 14

This block of commands is identical to Command Block 7, except that variable values are generated using long-term average stream flows.

```
"set AREA(" , iSWSeg, ") to ", AREA(iSWSeg)
"set DEPTH(" , iSWSeg, ") to ", DEPTH(iSWSeg)
"set WIDTH(" , iSWSeg, ") to ", WIDTH(iSWSeg)
"set VOL(" , iSWSeg, ") to ", VOL(iSWSeg)
"set KO2(" , iSWSeg, ",13) to ", KO2(iSWSeg,3)
```

Command Block 15

These two commands are issued only if the first simulation period has ended before detectable ground water loadings have arrived at the water body (i.e., Phase 1 ends more than a year before Phase 2 begins, as determined by SimSWEnd1 + 1 being less than SimSWInit2 - 1). These commands set up an interim simulation phase in which no loadings are specified.

```
"continue"
TEND
```

The value of TEND sets the end of the interim simulation period; it is set equal to the year before Phase 2 begins, or $(\text{SimSWInit2} - 1) * 12$ when expressed in months.

Control of simulation phase 2 – Phase 2 of the simulation proceeds from year SimSWInit2 until year SimSWEnd2. Groundwater loadings are updated periodically throughout Phase 2. For each new groundwater loading, Command Blocks 16 and 17 are issued defining a new simulation segment. When a new groundwater loading occurs at or after the end of simulation phase 2, then Command Block 18 is issued to terminate the Exams simulation.

Command Block 16

This block of commands is issued from subroutine InAqLoad; it is repeated for each reach in the water body network affected by groundwater loadings. For a particular reach, the index "iSResSeg" gives the Exams lower benthic compartment number. The index "3" is the ExamsIO array storage location for the present year's loading value. Loading is also indexed by "iChem." Individual loading commands are repeated for each separate chemical included in the HWIR simulation. In this HWIR application, the number of chemicals is always set to 1 (while this module treats mercury as three chemical components, loadings are generated by the other HWIR modules only for divalent mercury).

Each command is issued only if the fractional change in the variable from its previous setting is greater than Tolerance, which is set in ExamsIO to 0.001.

"set SEELD(", iSResSeg,",", iChem,",*") to ", SEELD(iSResSeg,iChem,3)

SEELD is the groundwater seepage loading of chemical "iChem" into compartment "iSResSeg," in kg/hr. It is calculated as the mean of the values specified in the groundwater loading file for the beginning and end of the current simulation segment.

Command Block 17

These two commands are issued from subroutine InAqLoad if the new groundwater loadings occur before the end of simulation phase 2.

"continue"
TEND

The variable "TEND" is calculated as 12 times the pointer "NextAquYear," which is the year for which the new groundwater loading is detected. TEND marks the end of the present simulation segment, in total months of elapsed simulation time.

Command Block 18

This command is issued from subroutine PreProc, and brings the Exams simulation to a close.

"exit"

4.0 MODULE VERIFICATION TESTING

Before application as a component of the HWIR production software, H-Exams was subjected to a series of tests to verify that the software accurately performs its prescribed computations. Model output was compared with different analytical solutions for a set of simplified test cases. These verification tests should be distinguished from model validation, in which model

predictions are compared against observed data. The core legacy model EXAMS has been applied and validated for various pesticides at different locations. The tests documented here were intended to verify that ExamsIO correctly implements EXAMS within the HWIR system. In addition, the tests verify that EXAMS accurately reproduces the expected analytical solutions.

All tests were done using a simplified water body network with four reaches. Two headwaters reaches (1 and 2) are connected to reach 3, which is connected to exiting reach 4. While all tests run the entire network, some focus on results in the first reach only. Analytical solutions based on the mass balance principal are used for loading, transport, and transformation tests. Basic chemical principals and formulas are used to test speciation and partitioning.

4.1 Test Water Body Network

The first test is to confirm that ExamsIO converts HWIR reach information into the proper EXAMS compartment structure with valid geometry. The HWIR reach type, length, and surface area are specified in the site layout file (SL.ssf). Depths and hydraulic coefficients are specified in the surface water file (SW.ssf). Stream width and depth are calculated from flow and the hydraulic coefficients.

The flow balance for this network is tested in the next section, but total flow results for reach 3 are used here. This stream reach experiences a steady flow of 3500 m³/day, or 0.0405 m³/sec. The depth multiplier and exponent are 0.5 and 0.4, giving stream depth of 0.139 m, which is passed to EXAMS through the batch command file "hwirexp.exe." The width multiplier and exponent are 10 and 0.25, giving a stream width of 4.49 m and a stream surface area of 10,335 m², which is also passed to EXAMS through the batch command file.

The surface water body network and geometry are summarized in the table below. A test simulation was run, and EXAMS Table 7 (Environmental input data: physical geometry) was checked. This comparison confirms that the network and physical geometry are being transferred correctly.

4.2 Test Water Balance

The next test is for a proper water balance. In the test network, the two headwaters reaches (1 and 2), flow into reach 3, which itself drains into reach 4 and exits the network. The reach connectivity is described by variables WBNRchNumRch, WBNRchRchIndex, and WBNRchRchFrac in the site layout file "SL.ssf." Constant baseflow and yearly runoff inflows from the watershed subbasins to the water body reaches are given in the watershed results file "ws.grf." These subbasin flows are mapped to the water body reaches by the site layout variables WBNRchNumWSSub, WBNRchWSSubIndex and WBNRchWSSubFrac, as described in section 2.2. Here, baseflow and runoff are each set to a constant value of 500 m³/day. Note that baseflow

Test Example: Physical Geometry

HWIR Reach #, Type	EXAMS Compartment #, Type	HWIR Water Body Geometry				EXAMS Volumes, m ³
		Length, m	Width, m	Depth, m	Surface Area, m ²	
1. Pond, Headwaters	1. Littoral	-	-	1.0	500	500
	2. Benthic			0.06		30
	3. Benthic			0.25		125
2. Wetland, Headwaters	4. Littoral	-	-	0.5	1000	500
	5. Benthic			0.08		80
	6. Benthic			0.30		300
3. Stream, Other	7. Littoral	2300	4.49*	0.139*	10,333**	1440
	8. Benthic			0.04		413
	9. Benthic			0.15		1550
4. Lake, Exiting	10. Epilimnion	-	-	1.0	10,000	10,000
	11. Hypolimnion			2.0	5,000	10,000
	12. Benthic			0.06		300
	13. Benthic			0.25		1250

* Calculated from flow and hydraulic coefficients.

** Calculated from length and width.

and runoff from subbasin 3 are split evenly between reach 3 and reach 4. Yearly precipitation and evaporation are given in the meteorological file. They were set at constant values of 81.75 cm/yr and 100 cm/yr, respectively, giving a net negative contribution to the water balance. Under baseflow conditions, equivalent stream widths were calculated from Eq. (1) to be 2.76 m, 2.76 m, 3.77 m, and 3.90 m for reaches 1 through 4. Equivalent lengths L_i' are calculated from surface areas for non-stream reaches 1, 2, and 4 assuming circular geometry:

$$L_r = 2 @ \sqrt{AS_r/p} \tag{61}$$

The equivalent lengths for reaches 1, 2, and 4 were 14.2 m, 20.1 m, and 63.7 m, respectively. The lengths and widths are multiplied by evaporation to give the evaporation loss.

The components of the water balance for this network are summarized in the table below. These inflows lead to total instream flows (in m³/day) of 1000, 1000, 3518, and 4019, for reaches 1 through 4, respectively.

HWIR Reach	Watershed Subbasin Flow Contributions			Waterbody Reach Flow Components, m ³ /day				
	WSSub #, frac	Baseflow m ³ /day	Runoff m ³ /day	Baseflow	BaseFlow Evap	Seepage	Runoff	Precip - Evap
1	1, 1.0	500	500	500	-0.11	500	500	-0.25
2	2, 1.0	500	500	500	-0.15	500	500	-0.50
3	3, 1.0	500	500	750	-23.8	774	750	-5.16
	4, 0.5	500	500					
4	4, 0.5					250	-0.68	251

These flow components can be compared with the hydrologic parameters summarized in EXAMS Table 5 (and elsewhere) to confirm that the flow inputs are being passed properly. Converting the units from the HWIR Seepage and Runoff flows in the preceding table confirms the EXAMS calculations for SEEPS and NPSFL. EXAMS variables RAIN and EVAP are confirmed with a units conversion from the HWIR values of 81.75 and 100 cm/yr to 68.13 and 83.3 mm/mo.

HWIR Reach	EXAMS Segment	NPSFL m ³ /hr	SEEPS m ³ /hr	RAIN mm/mo	EVAP mm/mo
1	1	20.8		68.13	83.3
	3		20.8		
2	4	20.8		68.13	83.3
	6		20.8		
3	7	31.3		68.13	83.3
	9		32.2		
4	10	10.4		68.13	83.3
	13		10.5		

While EXAMS does not provide output on the resultant compartment flows, the net flow balance can be confirmed with the successful testing of the conservative solids balance and chemical balance in the following two sections.

4.3 Test Solids Balance

As outlined in Section 2.3, the conservative solids balance employed in this version of H-Exams includes three loading terms. The largest source is generally watershed erosion. In this test, the erosion loading from each of the four watershed subbasins was set to 100,000 g/day in the watershed results file “ws.grf.” Erosion loads are mapped to water body reaches in the same manner as runoff using the variables WBNRchNumWSSub, WBNRchWSSubIndex, and WBNRchWSSubFrac in the site layout file “SL.ssf.”. The parameters and calculations leading to total watershed erosion by reach are summarized in the adjacent table.

HWIR Reach	Watershed Subbasin Solids Loading		Total Watershed Erosion Loading by Reach, g/day
	WSSub #, frac	Erosion g/day	
1	1, 1.0	100,000	100,000
2	2, 1.0	100,000	100,000
3	3, 1.0	100,000	150,000
	4, 0.5	100,000	
4	4, 0.5		50,000

Stream bank erosion can provide a significant contribution to the instream solids concentration. Lacking data necessary to calculate bank erosion mechanistically, H-Exams uses a simplistic approach. It is assumed that stream reaches incur an incremental 5 mg/L of solids due to bank erosion, and all other reaches incur an incremental 1 mg/L. The corresponding loadings are simply the product of total reach flow and the incremental concentration. The parameters and calculations leading to bank erosion loads by reach are summarized in the adjacent table.

HWIR Reach	Flow, m ³ /day	Bank Erosion Conc., mg/L	Bank Erosion Load, g/day
1	1000	1	1000
2	1000	1	1000
3	3518	5	17,590
4	4019	1	4019

Internal biotic production can add a small amount of solids to a reach. H-Exams calculates the incremental solids concentration added using a trophic index specified in the surface water input file "SW1.ssf," and the organic carbon fraction for biota specified in the site layout file "SL.ssf." The corresponding instream loadings are the product of the total reach flow and the incremental biotic solids concentration. The parameters and calculations leading to internal production loads by reach are summarized in the table below.

HWIR Reach	Flow, m ³ /day	Trophic Index	Biotic Carbon, mg/L	Biotic Solids, mg/L	Internal Production Load, g/day
1	1000	4	0.15	0.60	600
2	1000	6	0.50	2.0	2000
3	3518	2	0.06	0.24	844
4	4019	4	0.15	0.60	2411

In ExamsIO, these three sets of solids loadings are added to the water body reaches and transported downstream. The resultant TSS concentrations are the sum of the loadings to a reach (including all upstream loadings) divided by the total flow in the reach. The calculation of TSS is given in the table below, along with the values calculated by ExamsIO and passed to EXAMS. These results verify not only the H-Exams solids balance, but also the flow balance.

HWIR Reach	Waterbody Reach Solids Loading Components, g/day			Waterbody Reach TSS Calculation		ExamsIO, EXAMS TSS, mg/L
	Watershed Erosion	Bank Erosion	Internal Production	Flow, m ³ /day	TSS, mg/L	
1	100,000	1000	600	1000	101.6	102
2	100,000	1000	2000	1000	103.0	103
3	150,000	17,590	844	3518	106.0	106
4	50,000	4019	2411	4019	106.9	107

4.4 Test Loading and Conservative Chemical Transport

This next test is to confirm that chemical loadings are passed to EXAMS and transported through the EXAMS water body compartments properly. Four chemical loading pathways are employed – watershed runoff, direct source runoff, seepage inflow, and atmospheric deposition. Watershed runoff loadings from each of the four subbasins were set to 50 g/day over 20 years in the WS.grf file. These chemical loads are mapped to the water body reaches in the same manner as runoff volumes and erosion loads using the variables WBNRchNumWSSub, WBNRchWSSubIndex and WBNRchWSSubFrac in the SL.ssf file. The parameters and calculations leading to total watershed runoff loadings by reach are summarized in the adjacent table.

HWIR Reach	Watershed Subbasin Chemical Loading		Total Watershed Runoff Loading by Reach, g/day
	WSSub #, frac	Erosion g/day	
1	1, 1.0	50	50
2	2, 1.0	50	50
3	3, 1.0	50	75
	4, 0.5	50	
4	4, 0.5	50	25

Two direct source runoff loading pathways were specified in the source output file “SR.grf.” Both source loadings were set to 10 g/day over 10 years, and mapped to water body reaches 1 and 3 using variables WBNSrcLWSSubIndex and WBNSrcLWSSubFrac in the SL.ssf file. Two seepage loading pathway were specified in the aquifer output files “AQ1.grf” and “AQ2.grf.” The first loading was set to 18250 g/yr (50 g/day) for years 1 through 30, and mapped to water body reach 1 using variables WBNRchNumAQU, WBNRchAQUIndex and

WBNRchAquFrac. Likewise, the second aquifer loading was set to 1825 g/yr (5 g/day) for years 1 through 15 and mapped to stream reach 2.

Atmospheric deposition is described in the atmospheric output file “AR.grf.” Three sets of deposition fluxes are specified in this file – vapor wet deposition, particulate wet deposition, and particulate dry deposition. These were set to 0.1, 0.05, and 0.05 g/m²-day, respectively, for 10 years at four deposition locations. These deposition locations were mapped to water body reach 4 using variables WBNRchNumAir, WBNRchAirIndex, and WBNRchAirFrac in the SL.ssf file. Note that for each of the four flux locations within reach 4, the weighting fractions are set to 0.25. The deposition fluxes are summed and multiplied by the reach surface area, which is 10,000 m² for reach 4. The total atmospheric deposition to reach 4, then, is 2000 g/day.

The four loading vectors are summarized in the table below, along with the reach flow and total chemical concentrations obtained by dividing the total loadings at or above a reach by the total flow in the reach. The total chemical concentrations calculated within EXAMS and recorded in the surface water output file “SW1.grf” match these calculations very well, verifying the transfer of loadings to EXAMS, the flow balance and chemical advective transport within EXAMS, and the processing of EXAMS results into the surface water output file. It should be noted that the thermocline dispersion coefficient was set to a high value (1 cm²/sec) in the simulation in order to completely mix the epilimnion and hypolimnion. This was done so that a comparison could be made with the simple test calculation, which cannot handle layered water column reaches.

HWIR Reach	Waterbody Reach Chemical Loading Components, g/day				Waterbody Reach Chemical Calculation		EXAMS Water Column Conc., mg/L
	Watershed Runoff	Source	Seepage	Atmos. Deposition	Flow, m ³ /day	Conc., mg/L	
1	50	10	50		1000	0.110	0.110
2	50		5		1000	0.0550	0.0551
3	75	10			3518	0.0711	0.0711
4	25			2000	4019	0.566	0.565

4.5 Test Ionization

A series of simulations were run to test the pH effect on the speciation of organic acids and bases. Simulation output was compared with theoretical calculations based on equations presented in section 2.4.1.

Organic acids – H-Exams was first tested to verify that speciation of organic acids is being processed properly. Two dissociations were set up with pK_{a1} and pK_{a2} set to 6 and 8, respectively. A series of simulations were run with water body pH varying from 9 to 5. For each simulation, ExamsIO was run, generating the EXAMS chemical, environment, and batch run files. Then EXAMS was run interactively with these files, and the internal speciation results were examined from Exams Table 16. The results verify that EXAMS is receiving the speciation parameters and producing correct speciation results (see table below).

pH	Theoretical Species Ratios for $pK_{a1}=6, pK_{a2}=8$		EXAMS Speciation Calculations, percent		
	RH_3/RH_2^-	RH_2^-/RH^{2-}	RH_3	RH_2^-	RH^{2-}
9	10^{-3}	10^{-1}	0.0091	9.1	91.
8	10^{-2}	10^0	0.50	50.	50.
7	10^{-1}	10^1	8.3	83.	8.3
6	10^0	10^2	50.	50.	0.50
5	10^1	10^3	91.	9.1	0.0091

Organic bases – H-Exams was tested to verify that speciation of organic bases is being processed properly. Two dissociations were set up with pK_{b1} and pK_{b2} set to 8 and 6, respectively. A series

pH	Theoretical Species Ratios for $pK_{b1}=8, pK_{b2}=6$		EXAMS Speciation Calculations, percent		
	RH_3/RH_4^+	RH_4^+/RH_5^{2+}	RH_3	RH_4^+	RH_5^{2+}
9	10^3	10^1	100.	0.010	0.010
8	10^2	10^0	98.	0.98	0.98
7	10^1	10^{-1}	48.	4.8	48.
6	10^0	10^{-2}	0.98	0.98	98.
5	10^{-1}	10^{-3}	0.010	0.10	100.

of simulations were run with water body pH varying from 9 to 5. For each simulation, ExamsIO

was run, generating the EXAMS chemical, environment, and batch run files. Then EXAMS was run interactively with these files, and the internal speciation results were examined from EXAMS Table 16. The results verify that EXAMS is receiving the speciation parameters and producing correct speciation results (see table above).

4.6 Test Sorption

H-Exams uses partition coefficients to compute the sorption of a chemical to abiotic solids, biotic solids, and DOC. Coefficients for organic chemicals are processed in a different manner than those for metals, and are tested separately.

In the organic chemical partitioning test, K_{OW} was set to 400 and K_{OC} was set to 200 L/kg. The organic carbon fraction for biotic and abiotic suspended solids was set to 0.05, so that K_{PS} is 10 in all water column segments. The organic fraction for benthic solids was set to 0.005 for streams, 0.05 for ponds and lakes, and 0.50 for wetlands; the corresponding values of K_{PS} are 1, 10, and 100, respectively. From Eq. (31), the calculated K_{DOC} is 8 L/kg. DOC concentrations for streams, ponds and lakes, and wetlands were set to 1.25, 12.5, and 125, respectively, giving values of K'_{DOC} of 10^{-5} , 10^{-4} , and 10^{-3} , respectively. Finally, from Eq. (30), the calculated K_{PB} is 100. This is used for upper benthic segments only. These partition coefficients are summarized in the table below, along with the calculated concentrations from EXAMS. The relationships between the dissolved concentration and the chemical concentrations associated with DOC, solids, and biota exactly match the computed partition coefficients, verifying the treatment of sorption for organic chemicals

In the metals partitioning test, K_{PW} was set to 1000, K_{PSed} was set to 100, K_{PB} was set to 10, and K_{OC} was set to 1000 L/kg. The model internally equates K_{DOC} to K_{OC} . Given DOC concentrations of 1, 10, and 100 for streams, ponds and lakes, and wetlands, the calculated value of K'_{DOC} is 10^{-3} , 10^{-2} , and 10^{-1} , respectively. These partition coefficients are summarized in the table below, along with the calculated concentrations from EXAMS. The relationships between the dissolved concentration and the chemical concentrations associated with DOC, solids, and biota exactly match the computed partition coefficients, verifying the treatment of sorption for metals.

4.7 Test Volatilization

H-Exams uses the Whitman two-resistance model to calculate volatilization loss rate constants, as documented in section 2.4.5. EXAMS bases the gas transfer term on the wind-driven water vapor exchange velocity, which is calculated in the same way for all water body types. The liquid phase transfer term is based on the oxygen exchange (reaeration) velocity. Different sets of equations are used to calculate the reaeration velocity for flowing and stagnant water bodies. The volatilization equations are tested by manipulating input data for the test water body network and examining calculations for reach 1.

Organic Chemical Partitioning

Reach, Compartment	Partition Coefficients			EXAMS Concentrations			
	K_{DOC} L/L	K_{PS} L/kg	K_{PB} L/kg	C_D mg/L	C_{DOC} mg/L	C_S mg/kg	C_B mg/kg
1: Pond	focsed = 0.05, DOC = 12.5 mg/L						
water	10^{-4}	10		9.65e-2	9.65e-6	9.65e-1	-
upper sed	10^{-4}	10	10^2	9.95e-2	9.95e-6	9.95e-1	9.94e0
lower sed	10^{-4}	10		1.00e-1	1.00e-5	1.00e0	-
2: Wetland	focsed = 0.50, DOC = 125 mg/L						
water	10^{-3}	10		3.90e-2	3.90e-5	3.90e-1	
upper sed	10^{-3}	10^2	10^2	2.58e-2	2.58e-5	2.58e0	2.57e0
lower sed	10^{-3}	10^2		4.89e-5	4.89e-8	4.89e-3	
3: Stream	focsed = 0.005, DOC = 1.25 mg/L						
water	10^{-5}	10		1.62e-2	1.62e-7	1.62e-1	
upper sed	10^{-5}	1	10^2	3.46e-3	3.46e-8	3.46e-3	3.46e-1
lower sed	10^{-5}	1		7.36e-5	7.36e-10	7.36e-5	
4: Lake	focsed = 0.05, DOC = 12.5 mg/L						
epilimnion	10^{-4}	10		1.08e-2	1.08e-6	1.08e-1	
hypolimnion	10^{-4}	10		8.25e-3	8.25e-7	8.25e-2	
upper sed	10^{-4}	10	10^2	5.51e-3	5.51e-7	5.51e-2	5.50e-1
lower sed	10^{-4}	10		1.03e-4	1.03e-8	1.03e-3	

Metals Partitioning

Reach, Compartment	Partition Coefficients			EXAMS Concentrations			
	K_{DOC} L/L	K_{PS} L/kg	K_{PB} L/kg	C_D mg/L	C_{DOC} mg/L	C_S mg/kg	C_B mg/kg
1: Pond	DOC = 10 mg/L						
water	10^{-2}	10^3		8.80e-2	8.80e-4	8.80e+1	-
upper sed	10^{-2}	10^2	10	9.37e-2	9.37e-4	9.37e0	9.37e-1
lower sed	10^{-2}	10^2		9.92e-2	9.92e-4	9.92e0	-
2: Wetland	DOC = 100 mg/L						
water	10^{-1}	10^3		3.38e-2	3.38e-3	3.38e+1	
upper sed	10^{-1}	10^2	10	2.16e-2	2.16e-3	2.16e0	2.16e-1
lower sed	10^{-1}	10^2		4.10e-5	4.10e-6	4.10e-3	
3: Stream	DOC = 1 mg/L						
water	10^{-3}	10^3		1.59e-2	1.59e-5	1.59e+1	
upper sed	10^{-3}	10^2	10	1.52e-2	1.52e-5	1.52e0	1.52e-1
lower sed	10^{-3}	10^2		2.57e-4	2.57e-7	2.57e-2	
4: Lake	DOC = 10 mg/L						
epilimnion	10^{-2}	10^3		1.08e-2	1.08e-4	1.08e+1	
hypolimnion	10^{-2}	10^3		8.22e-3	8.22e-5	8.22e0	
upper sed	10^{-2}	10^2	10	7.81e-3	7.81e-5	7.81e-1	7.81e-2
lower sed	10^{-2}	10^2		6.29e-5	6.29e-7	6.29e-3	

Volatilization in streams – For the first volatilization test, a constant wind speed of 5 m/sec and water temperature of 20EC is specified. Inflow to reach 1 is 1000 m³/day. Hydraulic width coefficients a_{hyd_w} and b_{hyd_w} were set to 10 and 0.25, respectively; hydraulic depth coefficients a_{hyd_d} and b_{hyd_d} were set to 0.5 and 0.4. Molecular weight is 278, and Henry's law constant is set to 0.01 atm-m³/mole, which causes the overall volatilization rate to be controlled primarily by the liquid phase resistance.

From hydraulic equations (1) and (2), stream width and depth are 3.28 m and 0.084 m, which check out against the values for reach 1 in the EXAMS environment file. The reach current velocity is calculated as $Q/(86400 \times d \times W)$, or 0.0419 m/sec. To calculate reaeration velocity, the Owens formula is selected for depths less than 2 feet. From Eq. (46), K_{O_2} is 0.219 m/hr, which verifies the command "set KO2(1,13) to 21.8741" in the EXAMS batch run file (note that EXAMS expects KO2 in units of cm/hr). From Eq. (45), the given molecular weight yields a liquid phase transfer velocity of 0.0743 m/hr.

The wind speed of 5 m/sec from the meteorological file is multiplied by 0.5 to obtain the ground level (10 cm) wind speed of 2.5 m/sec, which verifies the wind speed entry in the EXAMS environment file. Using Eq. (44), the water vapor exchange velocity is calculated to be 28.6 m/hr. From Eq. (43), the given molecular weight yields a gas phase transfer velocity of 7.27 m/hr. This is multiplied by the term H/RT_k to give a net gas phase conductivity of 3.03 m/hr.

The liquid and gas phase transfer coefficients are combined in Eq. (42) to obtain the overall volatilization escape velocity of 0.0725 m/hr. Given the reach depth of 0.0824 m, the volatilization loss rate constant is 0.863 hr⁻¹. This loss rate constant corresponds to a half-life of 0.802 hours, which verifies the calculation of 0.80 hours in EXAMS Table 12.

For the second volatilization test, inflow is increased a thousand-fold to 10⁶ m³/day. From the hydraulic coefficients, depth and width are now 1.33 m and 18.44 m, and the current velocity is 0.472 m/sec. To calculate the reaeration velocity, the O'Connor-Dobbins formula is selected. From Eq. (48), K_{O_2} is 0.0975 m/hr, which verifies the command "set KO2(1,13) to 9.74146" in the EXAMS batch run file. The liquid phase transfer velocity is 0.0331 m/hr, which combined with the same gas phase transfer velocity of 7.27 m/hr gives an overall volatilization escape velocity of 0.0327 m/hr. Given the reach depth of 1.33 m, the volatilization loss rate constant is 0.0246 hr⁻¹. This loss rate constant corresponds to a half-life of 28.2 hours, which verifies the calculation of 28 hours in EXAMS Table 12.

For the third volatilization test, inflow is increased another ten-fold to 10⁷ m³/day. From the hydraulic coefficients, depth and width are now 3.35 m and 32.8 m, and the current velocity is 1.05 m/sec. To calculate the reaeration velocity, the Churchill formula is selected. From Eq. (47), K_{O_2} is 0.0982 m/hr, which verifies the command "set KO2(1,13) to 9.83165" in the EXAMS batch run file. The liquid phase transfer velocity is 0.0333 m/hr, which combined with the same gas phase transfer

velocity of 7.27 m/hr gives an overall volatilization escape velocity of 0.0333 m/hr. Given the reach depth of 3.35 m, the volatilization loss rate constant is 0.00994 hr⁻¹. This loss rate constant corresponds to a half-life of 69.7 hours, which verifies the calculation of 70 hours in EXAMS Table 12.

In order to test the gas phase resistance components of the model, these calculations were repeated for Henry's law constant values of 10⁻⁴ and 10⁻⁶. For H of 10⁻⁶, the gas phase resistance should control the overall volatilization rate; at 10⁻⁴, the gas and liquid phase resistances should contribute almost equally to the overall rate. The results of these tests, summarized in the table below, verify that the H-Exams stream volatilization routines are performing as expected.

Flow, m ³ /day	Depth, meters	H = 10 ⁻² atm-m ³ /mole		H = 10 ⁻⁴ atm-m ³ /mole		H = 10 ⁻⁶ atm-m ³ /mole	
		Calculated. t _{1/2} , hr	EXAMS t _{1/2} , hr	Calculated. t _{1/2} , hr	EXAMS t _{1/2} , hr	Calculated. t _{1/2} , hr	EXAMS t _{1/2} , hr
10 ³	0.084	0.80	0.80	2.7	2.7	193	193
10 ⁶	1.33	28	28	58	58	3080	3080
10 ⁷	3.35	70	70	146	146	7740	7740

Volatilization in ponds, wetlands, and lakes – Volatilization in stagnant water bodies is driven by wind speed. The theoretically-based equations from O'Connor (1983), summarized in section 2.4.5, were used in H-Exams. Ponds and wetlands were assumed to be in the intermediate size class, while lakes and bays were assumed to be in the large size class. The complex calculations are checked against two simpler empirical formulas that were summarized in EPA (1985). Banks (1975) developed the following expressions for KO₂ in shallow lakes applicable over a range of wind speeds:

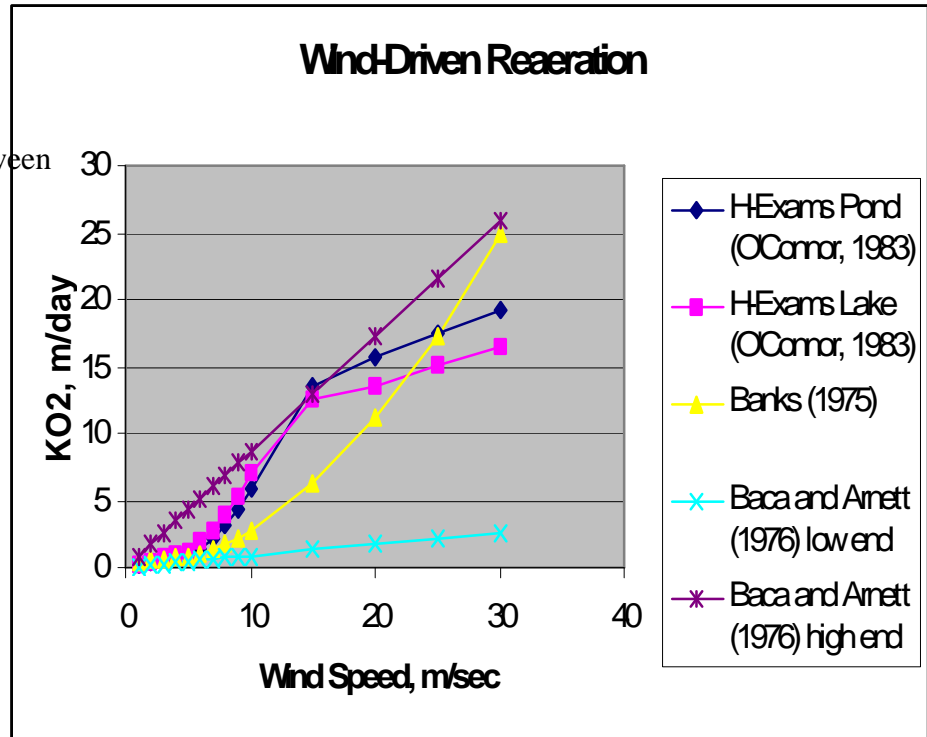
$$KO_2 = 0.362 @ W^{1/2} \quad \text{for } W < 5.5 \text{ m/sec} \quad (62)$$

$$KO_2 = 0.0277 @ W^2 \quad \text{for } W > 5.5 \text{ m/sec} \quad (63)$$

where KO₂ is the reaeration velocity, m/day, and W is wind speed, m/sec. Baca and Arnett (1976) used a linear expression to obtain a transfer coefficient for the mixed surface layer of lakes:

$$K_L = a_1 + a_2 @ W \quad (64)$$

where K_L is the surface transfer coefficient, day^{-1} , a_1 is a coefficient between 0.005 and 0.01, and a_2 is a coefficient between 0.0864 and 0.864. For purposes of this comparison, the reaeration velocity KO_2 was derived from this formula assuming that the mixed surface layer is 1 meter in depth. KO_2 values computed from these independent formulas for a range of wind speeds are summarized in the adjacent chart. The O'Connor equations implemented in H-Exams



give reaeration values within the range of the simpler formulas, providing a general verification of this model component. Most HWIR sites have average annual wind speeds between 3 and 6 m/second. In this range, the O'Connor equations track the Banks equations closely, as summarized in the table below.

Wind Speed, m/sec	Calculated Reaeration Velocity, m/day				
	H-Exams Pond	H-Exams Lake	Banks	Baca and Arnett, low	Baca and Arnett, high
1	0.19	0.24	0.36	0.091	0.87
2	0.37	0.48	0.51	0.18	1.7
3	0.55	0.71	0.63	0.26	2.6
4	0.74	0.97	0.72	0.35	3.5
5	0.93	1.2	0.81	0.43	4.3
6	1.5	1.9	1.0	0.52	5.2

Effect of ionization – H-Exams was tested to verify that speciation parameters from the HWIR chemical and site databases are affecting the volatilization rate properly. Henry’s Law constant was set at 0.01 atm-m³/mole, and wind speed was set at 5 m/sec. When no ionization is specified, the volatilization half-life for the neutral species is calculated to be 0.80 hr. For organic acids, one dissociation was set up with pK_{a1} varying between 9 and 5, and pH held constant at 7. For each simulation, ExamsIO was run, generating the EXAMS chemical, environment, and batch run files. Then EXAMS was run interactively with these files, and the internal speciation and volatilization results were examined from Exams Tables 16 and 12. The results verify that for organic acids, EXAMS is receiving the speciation parameters and producing correct speciation and volatilization results (see table below).

pK _{a1}	Theoretical Species Calculations for pH = 7		EXAMS Speciation and Volatilization Calculations		
	RH ₃ /RH ₂ ⁻	fraction RH ₃	fraction RH ₃	half life, hr	k _V /k _{V,neutral}
9	10 ²	0.99	0.990	0.81	0.99
8	10 ¹	0.91	0.909	0.88	0.91
7	10 ⁰	0.50	0.500	1.6	0.50
6	10 ⁻¹	0.0909	0.0909	8.8	0.091
5	10 ⁻²	0.0099	0.0099	81.	0.0099

For organic bases, one dissociation was set up with pK_{b1} varying between 9 and 5, and pH held constant at 7. The results verify that EXAMS is receiving the speciation parameters and producing correct speciation and volatilization results (see table below).

4.8 Test Transformation Reactions

The final set of tests check whether H-Exams is properly transferring transformation rate constants from the HWIR chemical database to EXAMS, and whether EXAMS is solving the resulting equations accurately. For each of the HWIR transformation reactions – hydrolysis, aerobic and anaerobic biodegradation, and reduction – a value of 0.693 day⁻¹ was specified for the rate constant in the water body chemical database “cpStream.ssf.” The corresponding EXAMS rate constants – neutral hydrolysis, water column biodegradation, sediment biodegradation, and reduction – should have a value of 0.0289 hr⁻¹ for the dissolved neutral species in the EXAMS chemical database “hwirexp1.chm.” Water column values of microbial biomass (BACPL) and reductant concentration (REDAG) should be set to 1.0 in the EXAMS environment file

pK _{b1}	Theoretical Species Calculations for pH = 7		EXAMS Speciation and Volatilization Calculations		
	RH ₃ /RH ₄ ⁺	fraction RH ₃	fraction RH ₃	half life, hr	k _v /k _{v,neutral}
9	10 ²	0.990	0.990	0.81	0.99
8	10 ¹	0.909	0.909	0.88	0.91
7	10 ⁰	0.50	0.500	1.6	0.50
6	10 ⁻¹	0.0909	0.0909	8.8	0.091
5	10 ⁻²	0.0099	0.099	81.	0.099

“hwirexp.env.” Benthic values of microbial biomass (BNBAC) should be set to values of 100 × porosity/dry density, (37.0 and 55.6 for the upper and lower sediment layers in the test network). As a result, chemical transformation half-lives calculated by EXAMS should be equal to 24 hours. Finally, chemical concentrations in any EXAMS compartment should be given by the following equation:

$$C_T = \frac{L_T}{Q \cdot k \cdot f_D \cdot V} \quad (65)$$

where C_T is the total chemical concentration, in mg/L, L_T is the total chemical loading, in g/day, Q is the total flow, in m³/day, k is the transformation rate constant, in day⁻¹, f_D is the chemical dissolved fraction, and V is the water column volume, in m³. For water column reactions in reach 1 of the example network ($L_T = 110$, $Q = 1000$, $f_D = 1$, and $V = 500$), C_T should equal 0.0817 mg/L when the rate constant is set at 0.693.

Eq. (65) can also be applied to dissolved pore water concentrations in benthic compartments. In the HWIR application, two sediment layers are simulated for each reach. Groundwater flow and loadings enter the underlying layer and are advected upward through the surficial layer and into the water column. H-Exams reports chemical concentrations in the upper sediment layer. To test those calculations, Eq. (65) can be modified and set up in series:

$$C_{D,BL} = \frac{L_{Seep}}{Q_{Seep} \left(\frac{k}{f_D} + V_{BL} n_{BL} \right)} \quad (66)$$

$$C_{D,BU} = \frac{Q_{Seep} C_{D,BL}}{Q_{Seep} \left(\frac{k}{f_D} + V_{BU} n_{BU} \right)} \quad (67)$$

where $C_{D,BL}$ and $C_{D,BU}$ are the dissolved pore water concentrations in the lower and upper sediment layers, in mg/L, L_{Seep} is the seepage loading in g/day, Q_{Seep} is the seepage flow, in m³/day, V_{BL} and V_{BU} are the total volumes of the lower and upper sediment layers, in m³, and n_{BL} and n_{BU} are the porosities of the lower and upper sediment layers, in L_w/L. For reach 1 of the test network, $L_{Seep} = 50$, $Q_{Seep} = 500$, $V_{BL} = 125$, $V_{BU} = 30$, $n_{BL} = 0.60$, and $n_{BU} = 0.50$. When f_D is 1 and k is 0.693, $C_{D,BL} = 0.0906$ mg/L and $C_{D,BU} = 0.0887$ mg/L.

Several simulations were conducted to confirm the proper transfer of rate constants to EXAMS. All passed the correct values to the EXAMS chemical file, and the resulting reaction half lives were calculated accurately by EXAMS. Finally, when the aerobic biodegradation rate constant is set to 0.693 day⁻¹, concentrations in the first reach are calculated by EXAMS to be 0.0818 mg/L, which is acceptably close to the value of 0.0817 mg/L derived from Eq. (65). Likewise, when the hydrolysis rate constant is set to 0.693 day⁻¹ (and the total loading is directly to the water column), EXAMS again calculates a water column concentration of 0.0818 mg/L. For the same hydrolysis rate constant, EXAMS calculates a dissolved concentration in the upper sediment layer of 0.0888 mg/L, which is acceptably close to the value of 0.0887 mg/L derived from Eq (66) and (67). Likewise, when the reduction rate constant or the anaerobic biodegradation rate constant is set to 0.693 day⁻¹, EXAMS calculates a dissolved concentration in the upper sediment layer of 0.0889 mg/L.

These and similar tests verify that H-Exams processes transformation reactions accurately.

REFERENCES

- Baca, R.G. and R.C. Arnett. 1976. A Limnological Model for Eutrophic Lakes and Impoundments. Battelle Pacific Northwest Laboratories.
- Banks, R.B. 1975. Some Features of Wind Action on Shallow Lakes, *Journal of Environmental Engineering Division, ASCE*, 101.
- Baughman, G. and D. Paris. 1981. Microbial Bioconcentration of Organic Pollutants from Aquatic Systems -- A Critical Review. *CRC Critical Reviews in Microbiology*. 8(3):205-228.
- Bowie, G.L., W.B. Mills, D.B. Porcella, C.L. Campbell, J.R. Pagenkopf, G.L. Rupp, K.M. Johnson, P.W.H. Chan, S.A. Gherini and C.E. Chamberlin. 1985. Rates, Constants, and Kinetics Formulations in Surface Water Quality Modeling. Second Edition. U.S. Environmental Protection Agency, Athens, GA. EPA-600/3-85-040.
- Burns, L.A., D.M. Cline, and R.R. Lassiter. 1982. Exposure Analysis Modeling System (EXAMS): User Manual and System Documentation. U.S. Environmental Protection Agency, Athens, GA. EPA-600/3-82-023.
- Burns, L.A. 1997. Exposure Analysis Modeling System (EXAMS II), User's Guide for Version 2.97.5. U.S. Environmental Protection Agency, Athens, GA. EPA/600/R-97/047.
- Chiou, C.T., R.L. Malcolm, T.I. Brintonn, and D.E. Kile. 1986. Water Solubility Enhancement of Some Organic Pollutants and Pesticides by Dissolved Fulvic Acids. *Environmental Science and Technology*, 20:502-508.
- Covar, A.P. 1976. Selecting the Proper Reaeration Coefficient for Use in Water Quality Models. Presented at the U.S. EPA Conference on Environmental Simulation Modeling, April 19-22, 1976. Cincinnati, Ohio.
- O'Connor, D.J. 1983. Wind Effects on Gas-Liquid Transfer Coefficients. *Journal of Environmental Engineering*, 109(3):731-752.
- Leopold, L.B. and T. Maddox. 1953. The Hydraulic Geometry of Stream Channels and Some Physiographic Implications. Professional Paper 252, U.S. Geological Survey, Washington, DC.
- Leopold, L.B., M.B. Wolman and J.P. Miller. 1964. *Fluvial Processes in Geomorphology*. W. H. Freeman and Co., San Francisco, CA.
- Liss, P.S. 1973. Processes of Gas Exchange Across an Air-Water Interface. *Deep-Sea Res.* 20:221-238.

Liss, P.S. and P.G. Slater. 1974. Flux of Gases Across the Air-Sea Interface. *Nature*, 247:181-184.

Servos, M.R., D.C.G. Muir, and G.R. Barrie. 1989. The Effect of Dissolved Organic Matter on the Bioavailability of Polychlorinated Dibenzo-p-dioxins. *Aquatic Toxicology*, 14(2):169-184.

U.S. Environmental Protection Agency. 1999. Partition Coefficients for Metals in Soil, Surface Water, and Waste. Prepared by Hydrologic, Inc., for U.S. Environmental Protection Agency, Office of Research and Development, Athens, GA.

Wetzel, R.G. 1983. *Limnology*, Second Edition. CBS College Publishing. p. 402.

Whitman, R.G. 1923. A Preliminary Experimental Confirmation of the Two-Film Theory of Gas Absorption. *Chem. Metallurg. Eng.* 29:146-148.